ASSESSMENT REPORT ON

MANGANESE

FOR DEVELOPING AMBIENT AIR QUALITY OBJECTIVES

105-05047

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Prepared by

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for

Alberta Environment

November 2004

Pub. No: T/775
ISBN No. 0-7785-3947-4 (Printed Edition)
ISBN No. 0-7785-3949-0 (On-line Edition)
Web Site: http://www3.gov.ab.ca/env/info/infocentre/publist.cfm

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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives[1] to support air quality management in Alberta. Alberta Environment currently has ambient objectives for more than thirty substances and five related parameters. These objectives are periodically updated and new objectives are developed as required.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations and the internally identified priority items by Alberta Environment, a three-year work plan ending March 31, 2004 was developed to review four existing objectives, create three new objectives for three families of substances, and adopt six new objectives from other jurisdictions.

In order to develop a new three-year work plan, a multi-stakeholder workshop was held in October 2004. This study was commissioned in preparation for the workshop to provide background information on alternative, science based, and cost effective methods for setting priorities.

This document is one of a series of documents that presents the scientific assessment for these adopted substances.

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[1] **NOTE**: The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the *Act*, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

ACKNOWLEDGEMENTS

The authors of this report would like to thank Dr. Long Fu of Alberta Environment for inviting them to submit this report. The authors are grateful for the help and guidance provided by Dr. Fu and his colleagues at Alberta Environment.

WBK & Associates Inc. would also like to acknowledge the authors who participated in the completion of this report:

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SUMMARY

Manganese (Mn) is an element that can exist in several valence states: 1,2,3,4,6,or 7, the most common being +2, +3 and +7. Manganese metal does not occur naturally however manganese may be found in over 100 minerals, primarily in the form of oxides, silicates and carbonates. It is also found in coal and crude oil. Manganese is used primarily in making steels and non-ferrous alloys. Other uses for manganese and manganese compounds include in the manufacturing of batteries, fertilizers, pesticides and ceramics, as a gasoline additive and as a dietary supplement. Manganese compounds are also used in animal feeds, pharmaceutical products, and wood preservatives and as catalysts.

Natural emission sources of manganese to the atmosphere are the result of erosion of soils and dusts. Anthropogenic activities that lead to the release of manganese and manganese compounds to air include industrial activities (such as alloy production and steel foundries) and combustion of fossil fuels (in power plants, coke ovens and automobiles). Combustion of MMT in gasoline of motor vehicles is reported to be one of the main anthropogenic sources of manganese in urban areas in Canada.

Manganese and manganese compounds exist in air associated with particulate matter, most of this particulate matter having a mass median equivalent diameter less than 5 µm. The processes governing the fate of manganese in the atmosphere are therefore the same processes as those that govern the transport and removal of particles from the atmosphere.

The primary end points of human toxicity associated with inhalation of inorganic manganese compounds related to particulate matter are neurotoxicity, reproductive dysfunction, and impairment of the respiratory system. Short-term exposures to animals are reported to cause: pneumonitis (rats exposed to 43,000 µg Mn oxide/m^3 for 6 hours/day over 10 days); increased susceptibility to pneumonia (mice exposed to 69,000 µg Mn oxide/m^3 for 3 hours/day over 1 to 4 days); respiratory effects (male rabbits exposed to 3,900 µg $MnCl_2$/m^3 for 6 hours/day and 5 days/week over 4 weeks); and decreased maternal pup retrieval latency (female mice exposed to 61,000 µg Mn oxide/m^3 for 7 hours/day and 5 days/week over 18 weeks).

Long-term (chronic) inhalation exposure to copper in the workplace is reported to cause: pneumonia (at 3,600 µg Mn oxide/m^3 for an unspecified exposure period); cough and decreased ling function (at 970 µg Mn salts and oxides/m^3 for an exposure period ranging from 1 to 19 years); decreased neurobehavioural performance (at 27 to 270 µg Mn oxides/m^3 for an exposure period ranging from 1 to 28 years); weakness, anorexia, ataxia (at 3,500 µg Mn/m^3 for an one year exposure period); and decreased fertility in males (at 145 to 970 µg Mn salts and oxides/m^3 for an exposure period ranging from 1 to 35 years). Long-term (chronic) inhalation exposure to monkeys is reported to produce hematological effects (100 µg Mn_3O_4/m^3 for 66 weeks).

The majority of trace metals present in ambient air are particle-bound. Sample collection schemes suitable for collection of trace metals, including manganese, follow methods appropriate for particulate matter measurement. Many analytical methods exist to characterize trace metals and each has its own advantages and disadvantages.

Urban settings – in which most air quality data are available for – are settings with higher metal concentrations in ambient air compared to rural settings. Ambient air data are available in central Edmonton and central Calgary for the period June 1991 to November 2000. Median and maximum manganese concentrations associated with $PM_{2.5}$ in ambient air were 0.0086 and 0.0833 $\mu g/m^3$ (central Edmonton) and 0.0089 to 0.0695 $\mu g/m^3$ (central Calgary).

1.0 INTRODUCTION

Alberta Environment establishes Ambient Air Quality Guidelines under Section 14 of the Environmental Protection and Enhancement Act (EPEA). These guidelines are part of the Alberta air quality management system (AENV, 2000).

The main objective of this assessment report was to provide a review of scientific and technical information to assist in evaluating the basis and background for an ambient air quality guideline for manganese. The following aspects were examined as part of the review:

- physical and chemical properties,
- existing and potential anthropogenic emissions sources in Alberta,
- effects on humans, animals, vegetation, and materials,
- ambient air guidelines in other Canadian jurisdictions, United States, World Health Organization and New Zealand, and the basis for development and use,
- characterization of risks to exposed receptors,
- monitoring techniques,

Important physical and chemical properties that govern the behaviour of manganese in the environment were reviewed and presented in this report. Existing and potential anthropogenic sources of manganese emissions in Alberta were also presented. Anthropogenic emissions are provided in Environment Canada's National Pollutant Release Inventory (NPRI).

Scientific information about the effects of manganese on humans and animals is reported in published literature and other sources. This information includes toxicological studies published in professional journals and reviews and information available through the US Agency for Toxic Substances and Disease Registry (ATSDR) and US Environmental Protection Agency's Integrated Risk Information System (IRIS). These sources provided valuable information for understanding health effects of manganese exposure.

Ambient air guidelines for manganese are used by numerous jurisdictions in North America for different averaging-time periods. These guidelines can be developed by using an occupational exposure level and dividing it by safety or adjustment factors, using cancer risk assessment procedures, or by using non-cancer risk assessment procedures. Examples of cancer and non-cancer risk assessment procedures are provided in WBK (2003). The basis for how these approaches are used by different jurisdiction to develop guidelines was investigated in this report.

Accurate measurement of trace metals, including manganese, in ambient air is often difficult in part because of the variety of substances, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. The United States Environmental Protection Agency (US EPA), National Institute of Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA) are the only organizations that provide documented and technically reviewed methodologies for determining the concentrations of selected trace metals of frequent interest in ambient and indoor air. These methods, which are generally accepted as the preferred methods for trace metal sampling and analysis, were reviewed and presented in this report.

2.0 GENERAL SUBSTANCE INFORMATION

Manganese (Mn) exhibits several valence states: 1,2,3,4,6,or 7 (Lide, 2002), the most common being +2, +3 and +7 (IPCS, 1981). Manganese metal does not occur naturally (ATSDR, 2000), however, manganese may be found in over 100 minerals, primarily in the form of oxides, silicates and carbonates (Lide, 2002; Pisarczyk, 1995). Manganese is also found in coal and crude oil (IPCS, 1981).

Manganese is used primarily in making steels and non-ferrous alloys (RSC, 1999). Other uses for manganese and manganese compounds include the manufacturing of batteries, fertilizers, pesticides and ceramics, as a gasoline additive and as a dietary supplement (Health Canada, 2001a). Manganese compounds are also used in animal feeds, pharmaceutical products, and wood preservatives and as catalysts (IPCS, 1981). Examples of inorganic compounds include manganese oxide, manganese dioxide, manganese chloride and manganese sulfate. Examples of organic compounds include MMT (methylcyclopentadienyl manganese tricarbonyl – a gasoline additive), manneb, mancozeb and mangafodibir (ATSDR, 2000).

Table 1 provides a list of important identification numbers and common synonyms for manganese and select manganese compounds.

2.1 Physical and Chemical Properties

The physical and chemical properties of manganese and select manganese compounds are summarized in Table 2.

2.2 Emission Sources and Ambient Levels

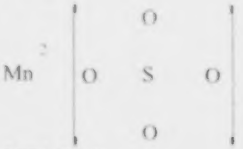
2.2.1 Natural Sources

Natural sources of manganese to the atmosphere are the result of the erosion of soils and dusts (ATSDR, 2000). Manganese may also be released to the air by volcanoes (Schroeder *et al.* cited in ATSDR, 2000).

2.2.2 Anthropogenic Sources

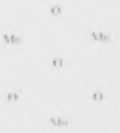
Anthropogenic activities that lead to the release of manganese and manganese compounds to air include industrial activities (such as alloy production and steel foundries) and combustion of fossil fuels (in power plants, coke ovens and automobiles, for example) (Health Canada, 2001a; ATSDR, 2000). According to Loranger and Zayed and Loranger *et al.* (cited in ATSDR, 2000), manganese emissions to air from automobiles, as a result of the combustion of MMT in gasoline, may be the one of the main anthropogenic sources of manganese in urban areas in Canada.

Table 1 Identification of Manganese and Select Manganese Compounds[a]

Property	Manganese	Manganese Chloride	Manganese Sulphate
Chemical Formula	Mn	$MnCl_2$	$MnSO_4$
Chemical Structure	Mn	Cl – Mn - Cl	
CAS Registry number	7439-96-5	7773-01-5	7785-87-7
RTECS number	OO9275000	OO9625000	OP1050000
UN Number	no data	no data	no data
Common Synonyms and Tradenames	Colloidal manganese Utaval Manganese fume Manganese metal Manganese-55 Manganese dust and fume	Manganese bichloride Manganese (II) chloride Managanese chloride, di- Manganese dichloride Manganous chloride scacchite	Manganese sulfate (1:2) Manganese (2+) sulfate (1:1) Manganes (II) sulfate Man-gro Sorba-spray manganese Sorba-spray Mn Sulphuric acid, manganese (II) salt (1:1) Sulphuric acid, manganese (2+) salt (1:1)

[a] all data from Genium (1999) unless otherwise stated

Table 1 Identification of Manganese and Select Manganese Compounds[a] (continued)

Property	Manganese Oxide	Manganese Dioxide	Manganese (II, III) Oxide
Chemical Formula	MnO	MnO_2	Mn_3O_4
Chemical Structure	Mn = O	O = Mn = O	
CAS Registry number	1344-43-0	1313-13-9	1317-35-7
RTECS number	OP0900000	OP0350000	OP0895000
UN Number	no data	no data	no data
Common Synonyms and Tradenames	C.I. 77726 Cassel Green Manganese Green Manganese Monooxide Manganese Monoxide Manganese Protoxide Manganese (II) oxide Manganese (II) oxide, mon- Manganosite Manganous Oxide Natural manganosite Nu-manese Rosensthiel	Black dioxide Black manganese dioxide Bog manganese C.I. 77728 C.I. Pigment Black 14 C.I. Pigment Brown 8 Cement Black Manganese Black Manganes (IV) oxide Manganese oxide Managanese peroxide Manganese superoxide Pyrolusite brown	Manganese oxide Manganomanganic oxide Trimanganese tetraoxide Trimanganese tetroxide Manganese tetroxide

[a] all data from Genium (1999) unless otherwise stated

Table 2 Physical and Chemical Properties of Manganese and Select Manganese Compounds[a]

Property	Manganese	Manganese Chloride	Manganese Sulphate
Molecular Weight (g/mol)	54.938	125.843	151.002
Oxidation State	0	+II	+II
Physical state	hard gray metal	pink trigonal crystals, hygroscopic	white orthorhombic crystals
Melting Point (°C)	1246	650	700
Boiling Point (°C)	2061	1190	850 (decomposes)
Density (g/cm^3)	7.3	2.977	3.25
Specific gravity (gas) (air =1)	no data	no data	no data
Vapour pressure	1mm Hg at 1292°C	no data	no data
Solubility in water	insoluble[b]	77.3 g/100g H_2O at 25°C	63.7 g/100g H_2O at 25°C
Solubility in other solvents	soluble in dilute acid solutions	soluble in pyridine, ethanol; insoluble in ethyl ether	insoluble in ether[b]
Henry's Law Constant ($atm.m^3/mol$)	no data	no data	no data
Octanol water partition coefficient (log K_{ow})	no data	no data	no data
Organic carbon partition coefficient (Log K_{oc})	no data	no data	no data
Odour threshold (mg/m^3)	odourless[b]	no data	no data
Bioconcentration factor in fish (log BCF)	no data	no data	no data
Conversion factors for vapour (at 25 °C and 101.3 kPa)	no data	no data	no data

[a] all data from Lide (2002) unless otherwise indicated

[b] Genium (1999)

Table 2 Physical and Chemical Properties of Manganese and Select Manganese Compounds[a] (continued)

Property	Manganese Oxide	Manganese Dioxide	Manganese (II, III) Oxide
Molecular Weight (g/mol)	70.937	86.937	228.812
Oxidation State	+II	+IV	mixed
Physical state	gray cubic crystals or powder	black tetrahedral crystals	brown tetrahedral crystals
Melting Point (°C)	1839	535 (decomposes)	1567
Boiling Point (°C)	no data	no data	no data
Density (g/cm^3)	5.37	5.08	4.84
Specific gravity (gas) (air =1)	no data	no data	no data
Vapour pressure	no data	no data	~ 0 mm Hg[b]
Solubility in water	insoluble	insoluble	insoluble
Solubility in other solvents	soluble in acid solutions	insoluble in nitric acid; soluble in dilute sulphuric acid[b]	soluble in hydrochloric acid
Henry's Law Constant ($atm.m^3/mol$)	no data	no data	no data
Octanol water partition coefficient (log K_{ow})	no data	no data	no data
Organic carbon partition coefficient (Log K_{oc})	no data	no data	no data
Odour threshold (mg/m^3)	no data	no data	odourless[b]
Bioconcentration factor in fish (log BCF)	no data	no data	no data
Conversion factors for vapour (at 25 °C and 101.3 kPa)	no data	no data	no data

[a] all data from Lide (2002) unless otherwise indicated

[b] Genium (1999)

Tables 3 and 4 summarize anthropogenic manganese emissions in Alberta, according to the National Pollution Release Inventory (NPRI) 2001 database (NPRI, 2002). Emissions of manganese and its compounds for Canada are presented in Appendix A. According to the NPRI database, the industrial sectors contributing the most to manganese emissions to air include the electric power sector, the primary metals industry, the pulp industry, the metals fabricating industry, and the petroleum and coal products industry. Most releases of manganese and its compounds are through stacks and other point sources, although some fugitive emissions and emissions during storage and handling exist.

2.2.3 Ambient Levels

Natural background levels of manganese in air are low, ranging from 0.006 $\mu g/m^3$ to 0.027 $\mu g/m^3$ (Georgii *et al.* cited in IPCS, 1991). In rural areas, manganese concentrations may range from 0.01 to 0.03 $\mu g/m^3$ (US EPA, 1973, cited in IPCS, 1981). In urban areas without important industrial sources of manganese, manganese levels may range from 0.01 to 0.07 $\mu g/m^3$ while near industrial sources, levels can range from 0.2 to 0.3 $\mu g/m^3$ to as high as 0.5 $\mu g/m^3$ (US EPA, 1994 cited in WHO, 2000; Pace and Franck cited in WHO, 2000). Data in ATSDR (2000) indicate that manganese concentrations in air have decreased from the years 1953 to 1982, most likely as the result of increased emissions control by industry (US EPA cited in ATSDR, 2001).

A study by Zayed *et al.* (cited in ATSDR, 2000) measured ambient levels of manganese in outdoor air at five locations in the Montreal area: at a gas station, at an underground parking lot, in downtown Montreal, near an expressway and near an oil refinery. The overall mean concentration (for all sites) of manganese was reported as 0.103 $\mu g/m^3$.

Ambient air data are available in central Edmonton and central Calgary for the period June 1991 to November 2000 (AENV, 2003). Median and maximum manganese concentrations associated with $PM_{2.5}$ in ambient air were 0.0086 and 0.0833 $\mu g/m^3$ (central Edmonton) and 0.0089 to 0.0695 $\mu g/m^3$ (central Calgary).

Table 3 Alberta Emissions of Manganese and Its Compounds According to NPRI (NPRI, 2002)

NPRI ID	Company	City	Province	Alberta Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
1036	Sheerness Generating Station	Hanna	AB	0.000	0.000	305.908	0.000	305.908
2284	TransAlta Corporation	Duffield	AB	3.217	0.000	208.356	0.000	211.573
2286	TransAlta Corporation	Duffield	AB	1.077	0.000	93.284	0.000	94.361
2282	TransAlta Corporation	Wabamun	AB	0.852	0.000	61.183	0.000	62.035
1106	AltaSteel Ltd.	Edmonton	AB	2.661	0.011	48.050	0.000	50.722
2875	Weyerhaeuser Company Ltd.	Grande Prairie	AB	0.142	13.191	31.164	0.000	44.497
2991	Weldwood of Canada	Hinton	AB	0.679	14.601	23.906	0.000	39.186
5283	Russel Metals Inc.	Edmonton	AB	0.000	0.000	17.000	0.000	17.000
0223	Daishowa-Marubeni International	MD of Northern Lights	AB	1.559	4.860	10.020	0.000	16.439
0001	Alberta Pacific Forest Industries Inc.	Boyle	AB	0.000	0.720	12.240	0.000	12.960
5390	City of Edmonton	Edmonton	AB	0.000	6.140	0.000	0.000	6.140
0267	Edmonton Power Inc.	Warburg	AB	0.593	0.000	0.000	0.000	0.593
5313	Foothills Steel Foundry Ltd.	Calgary	AB	0.000	0.000	0.000	0.000	0.300
5253	Cutler-Hammer	Airdrie	AB	0.160	0.000	0.000	0.000	0.160
2446	I-XL Industries Ltd.	Medicine Hat	AB	0.000	0.000	0.104	0.000	0.104
5682	Russel Metals Inc	Calgary	AB	0.066	0.000	0.000	0.000	0.066
0280	Dow Chemical Canada Incorporated	Fort Saskatchewan	AB	0.000	0.000	0.000	0.053	0.053
3707	Imperial Oil	Edmonton	AB	0.050	0.000	0.000	0.000	0.050
				11.056	39.523	811.215	0.053	862.147

Table 4 Alberta Air Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002)

NPRI ID	Company	City	Air Emission of Manganese and its Compounds (tonnes)					
			Stack and Point Sources	Storage and Handling	Fugitive	Spills	Other Non-Point Sources	Total
2284	TransAlta Corporation	Duffield	3.217	0.000	0.000	0.000	0.000	3.217
1106	AltaSteel Ltd.	Edmonton	0.725	0.985	0.951	0.000	0.000	2.661
0223	Daishowa-Marubeni International	MD of Northern Lights	1.559	0.000	0.000	0.000	0.000	1.559
2286	TransAlta Corporation	Duffield	1.077	0.000	0.000	0.000	0.000	1.077
2282	TransAlta Corporation	Wabamun	0.852	0.000	0.000	0.000	0.000	0.852
2991	Weldwood of Canada	Hinton	0.679	0.000	0.000	0.000	0.000	0.679
0267	Edmonton Power Inc.	Warburg	0.593	0.000	0.000	0.000	0.000	0.593
5253	Cutler-Hammer	Airdrie	0.000	0.000	0.160	0.000	0.000	0.160
2875	Weyerhaeuser Company Ltd.	Grande Prairie	0.142	0.000	0.000	0.000	0.000	0.142
5682	Russel Metals Inc	Calgary	0.000	0.000	0.066	0.000	0.000	0.066
3707	Imperial Oil	Edmonton	0.05	0.000	0.000	0.000	0.000	0.050
			8.894	0.985	1.177	0.000	0.000	11.056

3.0 ATMOSPHERIC CHEMISTRY AND FATE

Manganese and manganese compounds exist in the air associated with particulate matter (ATSDR, 2000), most of this particulate matter having a mass median equivalent diameter less than 5 μm (Lee *et al.* cited in IPCS, 1981). The processes governing the fate of manganese in the atmosphere are therefore the same processes as those that govern the fate of the released particulate matter. Manganese-containing particles are removed from the atmosphere by wet and dry deposition, with dry deposition playing a larger role (Turner *et al.*, US EPA cited in ATSDR, 2000). Larger particles are removed faster than smaller particles (US EPA cited in ATSDR, 2000). Manganese associated with particulate matter may react with sulphur dioxide and nitrogen dioxide, although proof of these reactions, other than in laboratory settings, has not been found (ATSDR, 2000).

MMT is converted quickly by photolysis (half life less than two minutes) to a mixture of solid manganese oxides and carbonates, with the solid consisting of organic compounds such as acids, esters and hydrocarbon polymers (Garrison *et al.*, Ter Haar *et al.* cited in ATSDR, 2000).

4.0 EFFECTS ON HUMANS AND ANIMALS

Present in all living organisms, manganese (Mn) is an essential element and a cofactor required for some enzymatic reactions. It can be found in urban air, water, and food (grains, cereals, tea) (ATSDR, 2000; Underwood, Keen and Leach cited in Goyer, 1996).

Manganese can be found in both inorganic and organic forms (ATSDR, 2000). This assessment evaluates the inorganic forms of Mn (e.g., manganese chloride ($MnCl_2$), manganese sulfate ($MnSO_4$), manganese acetate (MnOAc), manganese phosphate ($MnPO_4$), manganese oxide (MnO_2), and manganese tetroxide (Mn_3O_4)). Although some metals toxicity varies significantly depending on their oxidation state, there is not enough data to determine significant adverse effects associated with the difference forms of Mn (Mn(II), Mn(III), and Mn(IV)) (US EPA, 1996; ATDSR, 2000).

The toxicity of Mn can be determined by the route of exposure. When ingested, Mn is considered one of the least toxic trace metals; inhalation, however, can produce significant neurotoxicity (manganism) (US EPA, 1996).

The focus of this assessment was adverse health effects associated with inhalation of inorganic Mn, oral and dermal effects were not reviewed in detail. Due the lack of data, it was assumed Mn had similar levels of toxicity regardless of its oxidation state. The primary literature sources for this assessment were the Agency for Toxic Substances and Disease Registry (ATSDR, 2000), US Environmental Protection Agency (USEPA) Integrated Risk Information System (1996), and Klaassen *et al.* (1996).

4.1 Overview of Chemical Disposition

After inhalation, Mn is absorbed via the alveolar lining (EPA, 1993b cited in ATSDR, 2000); however, the percent absorbed is difficult to determine as it depends on the size of the particle inhaled (US EPA, 1996; ATSDR, 2000). Absorption of inhaled Mn was also reported to occur via the olfactory mucosa in rodents (Tjälve *et al.* cited in ATSDR, 2000; Roels *et al.* cited in US EPA, 1996 and ATSDR, 2000) and possibly in humans (Mergler *et al.* cited in US EPA, 1996 and ATSDR, 2000). If ingested, Mn is absorbed by the gastrointestinal tract (US EPA, 1984; Rozman and Klaassen, 1996); however, Mn is considered one of the least toxic trace metals by this route of exposure (US EPA, 1996). Inorganic Mn is not absorbed through the skin (ATSDR, 2000).

Metabolism of Mn appears to depend on its oxidation state (Mn(II), Mn (III), or Mn(IV)). The most naturally occurring forms are Mn(II) or Mn(IV) (ATSDR, 2000). Mn(III) appears to be the oxidation state for several enzyme systems in the body (Leach and Lilburn cited in US EPA, 1996 and ATSDR, 2000; Utter cited in ATSDR, 2000).

When ingested, a portion of absorbed Mn is removed by the liver and excreted in the bile before systemic circulation, this mechanism reduces potential toxic effects (Gregus and Klaassen, 1996). When absorption occurs via the respiratory tract, Mn does not pass through the liver before circulating throughout the body (US EPA, 1996). Once Mn enters the systemic

circulation it is transported in the plasma, distributed throughout the entire body and is commonly found in human tissue (including the brain), blood, serum, and urine (US EPA, 1984). Manganese concentrates in mitochondria, and thus is found in tissues with high amounts of mitochondria (pancreas, liver, kidneys and intestines) (Goyer, 1996). It crosses the blood-brain barrier and is retained longer in the brain than in the rest of the body (half life in the body is 37 days)(Goyer, 1996); Mn(II) accumulates in the mitochondria in parts of the brain associated with manganism (Mn toxicity) and neurological symptoms (ATSDR, 2000). Retention in tissues usually occurs with chronic, not acute exposures (ATSDR, 2000). Manganese (Mn) also binds to melanin and thus accumulates in cells containing melanin (Larsson, 1993, cited in Gregus and Klaassen, 1996).

The mechanism of Mn neurotoxicity toxicity of Mn has not yet been defined; however, Mn has been reported to affect cellular function such as: transport systems, enzyme activities, and receptor functions (Aschner and Aschner cited in ATSDR, 2000). It is thought that Mn(II) may increased autoxidation (resulting in increased free radicals, reactive oxygen species and other cytotoxic metabolites) and deplete cellular antioxidant defense mechanisms (Barbeau, Graham, Halliwell, Donaldson, Maines, Parenti *et al.*, Garner and Nechtman, Desole *et al.*, Verity cited in ATSDR, 2000). In addition to oxidation, Mn may also form complexes with other biological molecules (*e.g.*, bile, salts, proteins, nucleotides) (Gibbons *et al.* cited in ATSDR, 2000; ATSDR, 2000). *In Vitro* studies demonstrate that Mn (II) may affect mitochondrial enzyme activities and result in decreased energy production and neuronal degeneration (Gavin *et al.*, 1992, 1999, Brouillet *et al.*, Zheng *et al.* cited in ATSDR, 2000).

Althouhg the mechanism of toxicity is unclear, research has indicated that neuropathological bases for manganism involves the corpus striatum and the extrapyramidal motor system in the brain (Archibald and Tyree, Donaldson and Barbeau, Donaldson *et al.*, Eriksson *et al.*, 1987a, 1992 cited in US EPA, 1996). Manganese also produces lesions in the basal ganglia of human and non-human primate brains, primarily in the globus pallidus and sometimes, to a lesser extent, in the substantial nigra (Yamada *et al.*, Newland *et al.*, 1987, 1989, Newland and Weiss, Katsuragi *et al.* cited in ATSDR, 2000). Manganese also selectively destroys the dopaminergic receptor and neurons (Chu *et al.* cited in ATSDR, 2000). A summary of the neurological effects associated with Mn inhalation (manganism) is provided in Section 4.4.

Mn is rapidly eliminated in the bile and mostly excreted with the faeces; however, reabsorption does occur in the intestines (Goyer, 1996; Rozman and Klaasen, 1996). Some excretion also occurs via urine, breast milk, and sweat (US EPA, 1993b cited in ATSDR, 2000).

4.2 Genotoxicity and Carcinogenicity

No reliable studies regarding potential genotoxicity of Mn after inhalation were available (ATSDR, 2000).

4.3 Acute Effects

4.3.1 Acute Human Effects

Acute effects usually occur rapidly as a result of short-term exposures to high concentrations, and are of short duration – generally for exposures less than 24 hours (after Gallo, 1996). Acute exposure to manganese dioxide produces often-fatal manganese pneumonia (ATSDR, 2000). Inhalation of Mn is usually in the form of a respirable dust. The effects reported to occur in the respiratory system are similar to those associated with inhalation of respirable dust (ATSDR, 2000; US EPA, 1985d, cited in ATSDR, 2000) and include: inflammation, irritation and edema of the lungs, cough, bronchitis, pneumonitis, minor reduction of lung function, and occasionally pneumonia (Lloyd Davies cited in US EPA, 1996 and ATSDR, 2000; Abdel Hamid *et al.*, Akbar-Khanzadeh cited in ATSDR, 2000; Roels *et al.* cited in IRIS, 1996 and ATSDR, 2000). Thus, the effects reported may not be due to Mn toxicity, but due to particulate matter (US EPA, 1985d, cited in ATSDR, 2000).

4.3.2 Acute and Sub-Acute Animal Effects

Sub-acute effects usually occur as a result of exposures to moderately high that are of an intermediate duration – generally for exposures lasting a few days to about 21 days. Table 5 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature from acute animal studies. Table 6 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature from sub-acute animal studies.

Below is a summary of potential effects associated with acute and sub-acute Mn inhalation. Details regarding exposure concentrations, duration of exposure and animal species examined are included in Tables 5 and 6.

4.3.2.1 Respiratory Effects

Inflammation of the lungs was reported to occur after acute and sub-acute inhalation of Mn (Bergstrom cited in ATSDR, 2000; Camner *et al.*, Shiotsuka *et al.*, Suzuki *et al.* cited in US EPA, 1996 and ATSDR, 2000). Camner *et al.* (cited in US EPA, 1996 and ATSDR, 2000) reported no inflammation in rabbits after acute exposure to $MnCl_2$. Other sub-acute studies (rats, monkeys, and rabbits) reported no significant pulmonary effects after inhalation of Mn concentrations as high as 3.9 mg Mn/m^3 (Ulrich *et al.*, 1979a, 1979b, 1979c, Camner *et al.* cited in US EPA, 1996 and ATSDR, 2000).

4.3.2.2 Immunological Effects

An increased incidence of bacterial lung infections was associated with acute inhalation of Mn dusts (Maigetter *et al.* cited in ATSDR, 2000), while Lloyd Davies (cited in US EPA, 1996 and ATSDR, 2000) reported no increase in pnuemococci or streptococci infections.

4.3.2.3 Neurological Effects

Rodents appear to be less susceptible to manganese neurotoxicity than humans. Neurological effects appear to occur only at relatively high exposures (60 to 70 mg Mn/m^3) (Lown *et al.*, 1984).

Table 5 Examples of NOAELs and LOAELs Associated with Acute Manganese Inhalation (Experimental Animals)

Effects Reported[a]	Exposure Period	Air Concentration (mg Mn/m^3)	Species	Reference
Systemic:				
Pneumonitis, increased lung weight. Serious LOAEL	10d 6hr/d	43 MnO_2	Rats	Shiotsuka cited in ATSDR, 2000.
Hematological effects. NOAEL	10d 6hr/d	138 MnO_2	Rats	Shiotsuka cited in ATSDR, 2000.
Respiratory Effects in females. NOAEL	2hr	2.8 Mn_3O_4	Mice	Adkins *et al.* cited in ATSDR, 2000.
Respiratory effects. NOAEL	1hr	14 MnO_2	Guinea Pig	Bergstrom cited in ATSDR, 2000.
Immunological/Lymphoreticular:				
Increased susceptibility to pneumonia. NOAEL	1 to 4 d 3hr/d	69 MnO_2	Mice	Maigetter *et al.* cited in ATSDR, 2000.

[a] NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

Table 6 Examples of NOAELs and LOAELs Associated with Sub-Acute Manganese Inhalation (Experimental Animals)

Effects Reported[a]	Exposure Period	Air Concentration (mg Mn/m^3)	Species	Reference
Systemic:				
Mild respiratory inflammation. Less serious LOAEL	10 m 22hr/d	0.7 MnO_2	Monkey	Suzuki *et al.* cited in ATSDR, 2000.
Respiratory effects. NOAEL	9 m	1.1 Mn_3O_4	Monkey	Ulrich *et al.*, 1979b cited in ATSDR, 2000.
Respiratory Effects. NOAEL	9 m	1.1 Mn_3O_4	Rat	Ulrick *et al.*, 1979c cited in ATSDR, 2000.
Hematological Effects. NOAEL	9 m	1.1 Mn_3O_4	Rat	Ulrick *et al.*, 1979c cited in ATSDR, 2000.
Hepatic Effects. NOAEL	9 m	1.1 Mn_3O_4	Rat	Ulrick *et al.*, 1979c cited in ATSDR, 2000.
Respiratory Effects. NOAEL	4 wk 5d/wk 6hr/d	3.9 $MnCl_2$	Males rabbits	Camner *et al.* cited in ATSDR, 2000.
Neurological:				
NOAEL	9 m	1.1 Mn_3O_4	Monkey	Ulrick *et al.*, 1979c cited in ATSDR, 2000.
NOAEL	9 m	1.1 Mn_3O_4	Rat	Ulrick *et al.*, 1979c cited in ATSDR, 2000.
Decreased maternal pup retrieval latency. Serious LOAEL	18 wk 5d/wk 7hr/d[b]	61 MnO_2	Female mice	Lown *et al.*, 1984
Increased open-field behaviour. Serious LOAEL	16-32 wk 5d/wk 7hr/d	72 MnO_2	Male mice	Morganti *et al.* cited in ATSDR, 2000.
Reproductive Effects:				
Significantly larger litters than non-exposed dams. NOAEL	18 wk 5d/wk 7hr/d[b]	61 MnO_2	Mice	Lown *et al.*, 1984
Developmental Effects:				
Reduced neonatal scores and retard offspring growth that persisted into adulthood, depressed neonatal activity. Less serious LOAEL	16 wk before conception to Gd 17. 5d/wk 7hr/d[b]	49.1 1st 12 wks. 85.3 remaining wks MnO_2	Mice	Lown *et al.*, 1984

[a] NOAEL, Less serious LOAEL, and Serious LOAEL as identified by ATSDR (2000).

[b] Females were exposures 16 weeks before conception until day 17 of gestation.

4.3.2.4 Reproductive Effects

Male rabbits exposed acutely by intratrachial instillation[2] experienced slow (1 to 8 months) degeneration of the seminiferous tubules, loss of spermatogenesis and complete infertility (Chandra *et al.*, Seth *et al.* cited in ATSDR, 2000). No adverse reproductive effects were reported after pregnant rabbits were exposed sub-acutely to MnO_2 via inhalation (Lown *et al.*, 1984).

4.3.2.5 Developmental Effects

Lown *et al.* (1984) conducted a series of inhalation studies with females exposed for 18 weeks (16 weeks preconception up to gestational day 17). Pups either remained with the exposed mother to suckle, or were provided a non-exposed foster mother. Some pups were not exposed *In Utero*, only during suckling. Significant effects were observed in activity levels in all groups of pups. This was the only study identified which examined the potential inhalation effects of Mn in animals (US EPA, 1996).

4.4 Chronic Effects

4.4.1 Chronic Human Effects

Chronic effects generally occur as a result of long-term exposure to low concentrations, and are of long duration – generally as repeated exposures for more than 12 months (after Gallo, 1996). The majority of human inhalation exposure data available has been collected after occupational exposures. There are a number of limitations to be considered when using data from people exposed in the work place: i) the person exposed generally is a healthy, young to middle aged, male adult; ii) concurrent exposures to other chemicals are very likely; and, iii) the exposure concentrations are often difficult to define.

Table 7 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature.

Below is a summary of potential effects associated with chronic Mn inhalation. Details regarding exposure concentrations and duration of exposure are included in Table 7.

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[2] intratrachial instillation is a laboratory exposure technique which mimics inhalation. The absorption of particles are thought to occur via the upper and lower airways, and the gastrointestinal tract.

Table 7 Examples of NOAELs and LOAELs Associated with Chronic Manganese Inhalation (Human)

Effects Reported[a]	Exposure Period	Air Concentration (mg Mn/m^3)	Reference
Systemic:			
Pneumonia. Serious LOAEL	No data	3.6 MnO_2	Lloyd Davies cited in ATSDR, 2000.
Cough; decreased lung function. Serious LOAEL	1 –19 yr	0.97 Mn salts and oxides.	Roels *et al.* cited in ATSDR, 2000.
Hematological effects. NOAEL.	1 –19 yr	0.97 Mn salts and oxides.	Roels *et al.* cited in ATSDR, 2000.
Respiratory effects. NOAEL.	5.3 yr	0.18 Respirable dust. MnO_2	Roels *et al.* cited in ATSDR, 2000.
Endocrine effects. NOAEL	5.3 yr	0.18 Respirable dust. MnO_2	Roels *et al.* cited in ATSDR, 2000.
Neurological Effects:			
Postural sway with eyes closed. Less serious LOAEL.	1.1 – 15.7 yr	1.59 Total dust. MnO_2	Chia *et al.* cited in ATSDR, 2000.
NOAEL	12.7 yr. (mean)	0.051 Respirable dust.	Gibbs *et al.* cited in ATSDR, 2000.
Decreased reaction time; finger tapping. Less serious LOAEL	1-35 yr (2.6 median)	0.14 Total dust. MnO_2	Iregren cited in US EPA, 1996 and ATSDR, 2000.
Decreased neurobehavioural performance finger tapping; symbol digit; digit span; additions. Less serious LOAEL.	1–28 yr	0.027-0.27 Primarily MnO_2. MnO_x-Mn oxides.	Lucchini *et al.* cited in ATSDR, 2000.
Decreased performance on neurobehavioural exams. Less serious LOAEL.	11.5 yr (mean)	0.0967 MnO_2, Mn_3O_4	Lucchini *et al.* cited in ATSDR, 2000.

Table 7 Examples of NOAELs and LOAELs Associated with Chronic Manganese Inhalation (Human) (continued)

Effects Reported[a]	Exposure Period	Air Concentration (mg Mn/m^3)	Reference
Neurological Effects:			
Decreased motor function. Less serious LOAEL.	16.7 yr (Mean)	0.032 respirable dust.	Mergler *et al.* cited in US EPA, 1996 and ATSDR, 2000.
Altered reaction time, short-term memory, decreased hand steadiness. Less serious LOAEL.	1-19 yr	0.97 Mn salts and oxides	Roels *et al.* cited in US EPA, 1996 and ATSDR, 2000.
Impaired visual time, hand eye coordination, and hand steadiness. Less serious LOAEL	5.3 yr	0.179 Respirable dust. MnO_2	Roels *et al.* cited in US EPA, 1996 and ATSDR, 2000.
Psychomotor disturbances, weakness, pain. Serious LOAEL.	1-9 yr	6 MnO_2	Schuler *et al.* cited in ATSDR, 2000.
Weakness, anorexia, ataxia. Serious LOAEL.	1 yr	3.5	Whitlock *et al.* cited in ATSDR, 2000.
Reproductive:			
Decreased fertility in males. Serious LOAEL.	1-19 yr	0.97 Mn salts and oxides.	Lauwerys *et al.* cited in ATSDR, 2000.
Decreased fertility. NOAEL	Up to 35 yrs	0.145 Mean MnO_2	Jiang *et al.* cited in ATSDR, 2000.
Impotence, lack of sexual desire, abnormal ejaculation. Less serious LOAEL	Up to 35 yrs	0.145 Mean MnO_2	Jiang *et al.* cited in ATSDR, 2000.
Abnormal sperm. Serious LOAEL.	At least one yr.	6.5-82.3 Mn fumes.	Wu *et al.* cited in ATSDR, 2000.
Abnormal sperm. Serious LOAEL.	At least one yr.	0.14-5.5 MnO_2	Wu *et al.* cited in ATSDR, 2000.

[a] NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

4.4.1.1 Respiratory Effects

Respiratory diseases were reported to occur 30 times more frequently than normal in men exposed to manganese dust in the workplace (Goyer, 1996; Witschi and Last, 1996). Respiratory effects have also been reported in residents living near ferromanganese factories (Kagamimori *et al.*, Nogawa *et al.* cited in US EPA, 1996 and ATSDR, 2000; WHO cited in ATSDR, 2000).

4.4.1.2 Neurological Effects

Chronic industrial exposure to inhalation of manganese dioxide can result in chronic manganese toxicity (manganism), which affects the central nervous system (CNS). There is a great degree of individual variation in symptomatology of chronic Mn toxicity. Manganism is a neuropsychiatric disorder and is characterized initially by dull affect, sleep disturbances, irritability, difficulty walking, fine tremour, speech disturbances and compulsive behaviours (including running, fighting, singing), then a syndrome of psychological disturbances (hallucination, psychosis) can occur. Finally, a mask-like face, retropulsion or propulsion (difficulties controlling balance), and a "Parkinsonism-like" syndrome have been reported (Cook cited in ATSDR, 2000; Mena et al. cited in Goyer, 1996 and ATSDR, 2000) (Note: there are significant pathological differences between manganism and real Parkinsonism (Barbeau cited in US EPA, 1996 and ATSDR, 2000; Langston et al. cited in US EPA, 1996; Calne et al., Chu et al. cited in ATSDR, 2000). The CNS effects due to Mn exposure are the result of direct injury to parts of the brain. In some cases there was a slow recovery after exposure had ceased (Smyth et al., Shuqin et al. cited in ATSDR, 2000; Cotzias et al. cited in Goyer, 1996); however, in most cases, exposures have resulted in permanent neurological damage (Rodier cited in US EPA, 1996 and ATSDR, 2000; Cotzias et al., Huang et al. cited in ATSDR, 2000).

Manganism has been reported to occur in workers after inhalation of concentration levels ranging as low as 0.27 to 1 mg Mn/m^3 (Roels *et al.* cited in IRIS, 1996 and ATSDR, 2000; Iregren cited in US EPA, 1996 and ATSDR, 2000; Wennberg *et al.*, Chia *et al.*, 1993, 1995 cited in ATSDR, 2000; Mergler *et al.* cited in US EPA, 1996 and ATSDR, 2000; Lucchini *et al.* cited in ATSDR, 2000), with overt manganism occurring from 2 to 22 mg Mn/m^3.

4.4.1.3 Reproductive Effects

The following reproductive effects have been reported in men with manganism: impotence, loss of libido, changes in sperm liquifaction time, and decreased sperm count (Rodier cited in US EPA, 1996 and ATSDR, 2000; Schuler *et al.* cited in ATSDR, 2000; Mena *et al.* cited in Goyer, 1996 and ATSDR, 2000; Emara *et al.* cited in ATSDR, 2000; Cook *et al.* cited in US EPA, 1996 and ATSDR, 2000; Wu *et al.* cited in ATSDR, 2000). Impaired fertility was reported in men exposed in the workplace to Mn concentrations to low to produce frank manganism 0.97 mg/m^3 (Lauwerys *et al.* cited in ATSDR, 2000). A more recent assessment found no affect in fertility, but did report some incidences of reproductive dysfunction (Gennart *et al.* cited in US EPA, 1996; Jiang *et al.* cited in ATSDR, 2000). It could not be determined whether Mn was directly affecting reproductive organs, or whether the reproductive effects were a result of the neurological effects of manganism (ATSDR, 2000).

A unique study of both men and women in a community near a former manganese alloy production plant in South-western Quebec was identified (Mergler *et al.* cited in US EPA, 1996 and ATSDR, 2000; Bowler *et al.*, Beuter *et al.* cited in ATSDR, 2000). This study reported significant mood disturbances were in men older than 50 years with higher than normal Mn blood concentrations (Bowler *et al.* cited in ATSDR, 2000). Some motor performance tests were significantly worse with higher blood concentration, particularly in older men. This was not observed in women. Both men and women with elevated blood Mn concentrations had decreased performance in the leaning and memory tests (Mergler *et al.* cited in US EPA, 1996 and ATSDR, 2000).

4.4.1.4 Other Effects

Chronic inhalation of inorganic Mn can also affect cardiac function (Saric and Hrustic, Jiang *et al.* cited in ATSDR, 2000; Ramos *et al.*, 1996) and produce canalicular cholestasis (impaired bile secretion) (Molsen, 1996).

4.4.2 Chronic Animal Effects

Table 8 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature.

Below is a summary of potential effects associated with acute and sub-acute Co inhalation. Details regarding exposure concentrations, duration of exposure and animal species examined are included in Table 8.

Table 8 Examples of NOAELs and LOAELs Associated with Chronic Manganese Inhalation (Experimental Animals)

Effects Reported[a]	Exposure Period	Air Concentration (mg Mn/m^3)	Species	Reference
Systemic Effects:				
Hematological effects. NOAEL.	66 wk	0.1 Mn_3O_4	Monkeys	Coulston and Griffin cited in ATSDR, 2000.
Neurological:				
Altered DOPA levels.	2 yr 5d/wk 6hr/d	30 MnO_2	Female monkeys	Bird *et al.* cited in ATSDR, 2000.
NOAEL	66wk	0.1 Mn_3O_4	Monkeys	Coulston and Griffin cited in ATSDR, 2000.

[a] NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

4.4.2.1 Neurological Effects

Manganese has been reported to produce behavioural changes in mice and similar neurological changes in primates (Morganti *et al.*, Bird *et al.* cited in ATSDR, 2000).

For rodents, however, physiological differences and lack of adequate inhalation studies make it difficult to assess Mn neurotoxicity with respect to humans (US EPA, 1996). There are some experimental animal studies (inhalation and oral), which reported neurological effects (Chandra and Shukla, Deskin *et al.*, 1980, 1981, Gray and Laskey, Chandra *et al.*, Ali *et al.*, Chandra, Bird *et al.*, Bonilla and Prasad, Morganti *et al.*, Kristensson *et al.* cited in ATSDR, 2000; Eriksson *et al.*, 1987b cited in US EPA, 1996 and ATSDR, 2000; Komura and Sakamoto cited in ATSDR, 2000). Rodents appear to be less susceptible to manganese neurotoxicity than humans and do not demonstrate the impaired motor functions seen in human toxicity (Gray and Laskey, Komura and Sakamoto cited in ATSDR, 2000).

Studies of intravenous Mn exposure in primates reported neurological effects similar to those reported in human occupational exposures (Newland and Weiss, Olanow *et al.* cited in ATSDR, 2000; Newland cited in US EPA, 1996). Decreased concentration of dopamine in the brain was reported to occur in monkeys after chronic inhalation (Bird *et al.* cited in ATSDR, 2000).

4.4.2.2 Respiratory Effects

The same respiratory effects reported in humans have been reported in rats, monkeys, and hamsters with chronic inhalation (increased incidence of pneumonia, pulmonary emphysema, bronchiolar lesions) (Shiotsuka, Suzuki *et al.* cited in US EPA, 1996 and ATSDR, 2000; Moore *et al.* cited in US EPA, 1996). Intratrachial instillation of Mn also produced respiratory effects typical to exposure to Mn dust (Lloyd-Davies and Harding cited in US EPA, 1996).

4.5 Summary of Adverse Health Effects of Manganese Inhalation

The primary end points of toxicity associated with inhalation of inorganic manganese compounds in humans are: neurotoxicity; reproductive dysfunction; and, impaired respiratory system (most likely due to exposure to inhalable particulate matter).

Most significant to human exposures are the neurological effects associated with chronic inhalation exposures. Industrial exposure can result in chronic manganese toxicity (manganism) which affects the central nervous system (CNS) and can be characterized by: dull affect, sleep disturbances, irritability, difficulty walking, fine tremour, speech disturbances and compulsive behaviors (including running, fighting, singing), then a syndrome of psychological disturbances (hallucination, psychosis) can occur. Finally, a mask-like face, balance and movement problems, and a "Parkinsonism-like" syndrome can occur. Occupational studies demonstrate that inhalation of low levels of Mn produces neurotoxicity.

Studies of men with manganism have also revealed adverse reproductive effects (impotence, loss of libido, changes in sperm liquifaction time, and decreased sperm count). Impaired fertility was reported in men exposed in the workplace to Mn concentrations too low to produce frank manganism. Chronic inhalation of inorganic Mn can also affect cardiac function.

Acute and sub-acute inhalation of Mn in animal studies (rats, monkeys, and rabbits) produced no significant pulmonary effects. An increased incidence of bacterial lung infections was associated with acute inhalation of Mn dusts. Rodents appear to be less susceptible to manganese neurotoxicity than humans. A single exposure to male rabbits resulted in a slow degeneration of the seminiferous tubules, loss of spermatogenesis and complete infertility. No adverse reproductive effects were reported after pregnant rabbits were exposed sub-acutely via inhalation; however, significant developmental effects were reported in the pups exposed maternally. Chronic inhalation in animals has been reported to produce similar respiratory effects seen in people (increased incidence of pneumonia, pulmonary emphysema, bronchiolar lesions).

5.0 EFFECTS ON MATERIALS

Most of the metals emitted to the atmosphere are associated with particulate matter at ambient temperatures or – less frequently – in the vapor state. Metal oxides tend to be adsorbed to or associated with particles. This is the case for numerous individual metals (after WBK, 2003):

- Arsenic occurs naturally in soil and minerals and may enter the air as wind-blown dust particles. Arsenic released from combustion processes is usually attached to very small particles.

- Cobalt is probably emitted in the particulate form to the air, since compounds of cobalt are not usually volatile.

- Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter.

- Elemental manganese and inorganic manganese compounds have negligible vapor pressures but may exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils.

- Nickel releases to the atmosphere are mainly in the form of aerosols that cover a broad spectrum of sizes. Nickel from power plants and smelters tend to be associated with small particles.

- Vanadium generally enters the atmosphere as an aerosol. Vanadium attributed to combustion of residual fuel oils and coal is generally in the form of vanadium oxides and contributes to approximately two-thirds of the atmospheric vanadium.

- Zinc occurs in the environment mainly in the divalent (+2) oxidation state. It is found in the atmosphere at the highest concentrations in small particles.

Thus the predominant issue with respect to ambient emissions of metals negatively affecting material surfaces will be because of its association with deposited airborne particulate matter. Excluding acidic particles, deposition of airborne particles on material surfaces can cause soiling (Baedecker *et al.*, 1991). In addition, particles deposited on a surface can adsorb or absorb acidic gases (e.g. SO_2 and NO_2), thus serving as nucleation sites for these acidic gases. This may accelerate physical and chemical degradation of material surfaces that normally occur when materials are exposed to environmental factors such as wind, sun, temperature fluctuations, and moisture.

Haynie and Lemmons (1990) described soiling as the contrast in reflectance of particles on a substrate compared to the reflectance of a bare substrate. Soiling of materials is a concern because it results in more frequent cleaning and repainting, thereby reducing its lifetime usefulness and increasing costs associated with maintenance of the materials.

Haynie (1986) reported that it is difficult to determine the amount of deposited particles that cause an increase in soiling. However, Haynie (1986) indicated that soiling is dependent on the particle concentration in the ambient environment, particle size distribution, and the deposition rate and the horizontal or vertical orientation and texture of the surface being exposed. Schwar (1998) reported that the buildup of particles on a horizontal surface is counterbalanced by an equal and opposite depletion process. The depletion process is based on the scouring and washing effect of wind.

6.0 AIR SAMPLING AND ANALYTICAL METHODS

6.1 Introduction

Accurate measurement of trace metals in ambient air is often difficult, in part because of the variety of substances, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. The United States Environmental Protection Agency (US EPA, 1999a), National Institute of Occupational Safety and Health (NIOSH, 1994), and Occupational Safety and Health Administration (OSHA, 2002a; 2002b) are the only organizations that provide documented and technically reviewed methodologies for determining the concentrations of selected trace metals of frequent interest in ambient and indoor air. It is these methods, which are presented here, that are generally accepted as the preferred methods for trace metal sampling and analysis.

6.2 Sampling Methods

The majority of trace metals present in ambient air are particle-bound. Therefore, the sample collection schemes appropriate for the collection of trace metals follow the methods appropriate for particulate matter measurements. There are many sampling systems available for particulate matter measurements, each with its own advantages and disadvantages. Only some, however, are capable of collecting samples that are suitable for elemental analysis. The major prerequisites in selecting a sampling system are to determine what size range of particles are to be monitored, what trace metals are of interest, and the appropriate method of analysis. The analytical method selection is very important, because only some methods are compatible with each sampling system. The available documented and technically reviewed methods include high volume samplers for collecting TSP (total suspended particulate with aerodynamic diameters less than 100 μm) and PM_{10} (particulate matter with aerodynamic diameters less than 10 μm) and low volume samplers for collecting PM_{10} and $PM_{2.5}$ (particulate matter with aerodynamic diameters less than 2.5 μm) utilizing dichotomous and Partisol samplers. Each of these samplers has the ability to collect particulate matter uniformly across the surface of the filters and they are commonly used in Alberta. They can be used to determine average ambient particulate matter concentration over the sampling period, and the collected material can subsequently be analyzed for inorganic metals and other materials present in the collected sample. Some of the advantages and disadvantages associated with the sampling options are summarized in Table 9.

6.2.1 Hi-Vol Sampler

The primary method used to sample airborne particulate matter in a volume of ambient air with the objective of identifying and quantifying the inorganic metals present has historically been the high volume (hi-vol) sampler (US EPA, 1999a). Air is drawn into the sampler and through a glass fiber or quartz filter by means of a blower (typically at a rate of 1.13 to 1.70 m^3/min), so that particulate material collects on the filter surface. If a 10 μm size-selective inlet is used, only particles of 10-μm size and less enter the sampling inlet and are collected on the downstream filter. Without the inlet, particles of 100-μm size and less are collected. When glass fiber filters

Table 9 Method Advantages and Disadvantages

Method	Advantages	Disadvantages
Sampling Methods		
	Reference method	Many interferences
	Well documented applications	Cannot sample fine fraction
Hi-Vol Sampler	Collects a substantial amount of material	Not compatible with some analytical techniques
	Lower concentrations of metals can be detected	Inconvenient
	Reference method	Low loadings
Dichotomous Sampler	Collects two size fractions	Requires a higher concentration
	Allows use of various filter media	
Partisol Sampler	Simple and convenient	Low loadings
	Allows use of various filter media	Requires a higher concentration
	Simple, convenient and inexpensive	Low loadings
Mini-Vol Sampler	Allows use of various filter media	Requires a higher concentration
		Limited documented applications
Analytical Methods:		
Flame Atomic Absorption Spectroscopy	Easy to use	Higher concentration required
	Extensive applications	Sample dissolution is required
	Low detection limits	One element at a time
	Well documented applications	Limited working range sample
Graphite Furnace Atomic Absorption Spectroscopy	Lower detection limits than FAA	Low sample throughput
		One element at a time
		More operator skill
		Sample dissolution is required
X-Ray Fluorescence Spectroscopy	Multi-element	Standard/sample must match closely
	Non-destructive	Matrix offsets and background
	Minimal sample preparation	impurities may be a problem
	Multi-elemental	More expensive (~120K)
Inductively Coupled Plasma Spectroscopy	High sample throughput	Sample dissolution is required
	Well documented applications	Other elements can interfere
	Intermediate operator skill	
	Linear range over 5 orders of magnitude	
Inductively Coupled Plasma/Mass Spectroscopy	Multi-elemental	Most expensive (~250K)
	Low concentrations	Limited documented applications
	Isotopic analysis	Sample dissolution is required
	Intermediate operator skills	
Proton Induced X-Ray Emission Spectroscopy	Multi-element	Standard/sample must match closely
	Non-destructive	Matrix offsets and background
	Minimal sample preparation	impurities may be a problem
	Multi-element	Some elemental interferences
Instrumental Neutron Activation Analysis Spectroscopy	Non-destructive	Standard sample matrix corrections
	Minimal sample preparation	Required access to research nuclear reactor
	Detection limit to ppt range	
	High sample throughput	
	Well documented applications	
Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy	Chemical and physical characterization	Poor sensitivity
	Non-destructive	Time consuming
	Minimal sample preparation	Limited documented applications

are used, particles 100 μm or less are ordinarily collected. With a size-select inlet, particles 10 μm or less are collected on quartz filters. The hi-vol's design causes the particulate matter to be deposited uniformly across the surface of the filter. The mass concentration of suspended particulates in the ambient air is computed by measuring the mass of collected particulates and the volume of air sampled. After the mass is measured, the filter is ready for extraction to determine the metal concentration.

Because of its higher flow rates, the hi-vol collects more material so lower ambient concentrations of inorganic materials can be detected (assuming identical filter medium and analysis technique). The major interferences in suspended particulate matter determination are collection of large extraneous objects (e.g., insects), collection of liquid aerosols and gas or vapours that may react with some filter types and/or collected materials to add artificial weight (ARPEL, 1998). The high-volume sampling technique has been recommended as the method for sampling ambient particulate matter by most air quality agencies including the US EPA and Environment Canada. As delineated later, airborne particulate matter retained on the filter may be examined or analyzed chemically by a variety of methods including inductively coupled plasma (ICP) spectroscopy, inductively coupled plasma/mass spectroscopy (ICP/MS), flame atomic absorption (FAA) spectroscopy, graphite furnace atomic absorption (GFAA) spectroscopy, and instrumental neutron activation analysis (INAA).

6.2.2 Dichotomous Sampler

Dichotomous samplers are used to sample airborne particulate matter in coarse (2.5 to 10 μm) and fine (<2.5 μm) size fractions. In dichotomous samplers, ambient air is drawn at a flow rate of approximately 1 m^3/hr. The coarse fraction of particulate matter is accelerated into the central collection filter while the fine fraction is drawn onto a second collection filter. Particles that are < 10 μm are collected via a 10 μm inlet and separated into fine (<2.5 μm) and coarse (2.5 to 10 μm) fractions by a virtual impactor. In recent literature of ambient air particulate sampling and elemental analysis, the duration of sampling ranges from 12 to 24 hours depending upon experimental design and amount of ambient particulate present (US EPA, 1999). The mass concentration of airborne particles within each size range is determined gravemetrically. The detection limit for the method depends on the sensitivity of the analytical balance utilized for the gravimetric determination and the volume of air sampled. The dichotomous sampler has the advantage of collecting two fractions so that information can be obtained about total PM_{10} and/or both of the two fractions. In addition, the dichotomous sampler operates at a low flow rate, which allows the use of filter media that would otherwise quickly clog at high-volume flow rates. The particles are collected on Teflon filters and once at the laboratory are analyzed by X-ray fluorescence (XRF) spectrometry, proton induced X-ray emissions (PIXE) spectrometry, or instrumental neutron activation analysis (INAA).

6.2.3 Partisol Sampler

The Ruppecht and Patashnick (R&P) Low-Volume Partisol Air Sampler is a microprocessor-controlled manual sampler with a unique set of features that make it a suitable platform for measuring particulate and other constituents found in the atmosphere (US EPA, 1999a).

Ambient air is drawn through a low flow (16.7 L/min) PM_{10} or $PM_{2.5}$ inlet where particle size selection takes place. The particulate-laden air is then directed through a collection filter composed of either quartz, Teflon-coated glass, or Teflon where the particulate matter is collected. A mass flow control system maintains the sample flow through the system at the prescribed volumetric flow using information from sensors that measure the ambient temperature and ambient pressure. The sample filter is conditioned and weighed both before and after sample collection to determine the amount of mass collected during the sampling period. The airborne particulate collected on the 47-mm filter in the Partisol Sampler may be subjected to a number of post-collection chemical analytical techniques to ascertain the composition of the material caught by the filter. Appropriate techniques include X-ray fluorescence (XRF) spectrometry, proton induced X-ray emissions (PIXE) spectrometry, and instrumental neutron activation analysis (INAA). The type of filter media should be compatible with the analytical method used.

6.2.4 Alternative Sampling Methods

In addition to the documented and technically reviewed methodologies for collecting trace metals in ambient air there are alternative methods. One such method is the Portable Minivolume Air Sampler (MiniVol) made by Airmetrics (Airmetrics, 1998). The MiniVol works by drawing air through a size-selective impactor that removes the unwanted larger sizes of particulate and captures the smaller sizes on a filter. It has a twin cylinder vacuum pump that is designed to pull air at 5 L/min (at standard temperature and pressure) through an impactor that is capable of removing particles larger than the cut-points of either 10 μm or 2.5 μm. This active sampler is operated by the principle of inertial impaction using a single stage impactor with a filter. In this device, the particle-laden air is accelerated through one nozzle and the exiting jet impinges upon a plate. The impactor dimensions are chosen such that particles smaller than the desired cut-point follow the streamlines as they bend at the impaction plate, while the larger particles with sufficient inertia depart from the streamlines and impact against the plate. The elemental and morphological properties of the deposited material are later analyzed using an appropriate technique (Jones *et al.*, 1998; Tropp *et al.*, 1998). Environment Canada uses the MiniVol as a saturation sampler and they have been used extensively in several parts of Alberta under a variety of climatic conditions (Alberta Health, 1997).

6.3 Analytical Methods

Many analytical methods exist to characterize trace metals collected on a filter substrate and each has its own attributes, specificities, advantages and disadvantages. Though several methods are multi-species (able to quantify a number of different chemical components simultaneously) no single method is sufficient to quantify both the majority of the collected particulate matter mass and those trace elements which may be of interest. The type of analytical technique used is generally dictated by the specific sampling method employed to collect the particulate matter. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique and vice-versa. Most importantly, the choice of analytical method will depend on the metals of interest and the detection limits desired. Some of the advantages and disadvantages associated with the analytical options are summarized in Table 9. While factors such as element specificity and sensitivity are critically important, considerations such as cost

and throughput (the number of samples and number of elements to be determined per sample) are also significant.

6.3.1 Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) has occasionally been used as the primary method for metals determination (Beceriro-Gonzalez *et al.*, 1997), but is more commonly used as a supplementary technique for elements not amenable to analysis by one of the multi-elemental techniques described later (Kowalczyk *et al.*, 1982; Rizzio *et al.*, 2000). In this method, trace metals in a particulate matter sample are extracted by either a hot acid or microwave extraction procedure into a solution and subsequently vaporized in a flame. A light beam with a wavelength matching the absorption wavelength of the metal of interest passes through the vaporized sample. The light attenuated by the sample is then measured and the amount of the metal present is determined using Beer's Law (Koutrakis and Sioutas, 1996).

AAS describes both flame atomic absorption (FAA) spectroscopy and graphite furnace atomic absorption (GFAA) spectroscopy (US EPA, 1999a). The two atomic absorption analyses options are similar in that the measurement principle is the same. However, they differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is absorbed. Each element absorbs light at a characteristic wavelength and, therefore, analysis for each element requires a different light source. This means only one element can be determined at a time. In FAA, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GFAA, a graphite furnace electrothermal atomizer is used.

AAS has the advantage of being able to accurately measure difficult elements such as cadmium, lead, zinc and magnesium. However, the necessary dissolution of collected particulate and the manipulation of a solution of trace elements is not a trivial thing. Furthermore, AAS can only analyze one element at a time thus rendering the analysis of an extensive set of elements prohibitively time consuming. The analytical technique is also destructive and requires that the sample be extracted or digested for introduction into the system in solution. The detection limit of GFAA is typically about two orders of magnitude better than FAA (US EPA, 1999a). High-volume samplers are typically used for sampling when FAA or GFAA analysis is planned.

6.3.2 X-Ray Fluorescence Spectroscopy

In X-Ray Fluorescence (XRF) (Dzubay and Stevens, 1975; Dzubay, 1977; Lewis and Macias, 1980; Price *et al.*, 1982; Dzubay *et al.*, 1988; Glover *et al.*, 1991; Schmeling *et al.*, 1997) a beam of X-rays irradiates the particulate matter sample. This causes each element in the sample to emit characteristic X-rays that are detected by a solid-state detector or a crystal spectrometer. The characteristic X-ray is used to identify the element and the intensity is used to quantify the concentration of the measured element. X-ray fluorescence spectrometry (including energy dispersive and wavelength dispersive modes) can be accurately used for all elements with atomic weights from 11 (sodium) to 92 (uranium). Furthermore, multiple elements can be determined simultaneously.

This method has the advantages of being non-destructive, requiring minimal sample preparation, providing immediate results and having low equipment cost. However, the detection limit is higher than other analysis techniques. In addition, it requires a thin collection deposit (i.e. 10 to 50 $\mu g/cm^2$) and it involves complex matrix corrections. Elements lighter than aluminum are often difficult to determine because of their low fluorescent yields and particularly because of the strong absorption of fluorescent X-rays by the substrate on which they are collected (US EPA, 1999a). Because high-volume samplers utilize quartz-filters that cause high background when employing XRF, analysis by XRF usually requires Teflon or Nylon filters used in the dichotomous or the Partisol samplers.

6.3.3 Inductively Coupled Plasma Spectroscopy

In Inductively Coupled Plasma (ICP) Spectroscopy analysis, the particulate matter sample is excited using an argon plasma torch (ARPEL, 1998; US EPA, 1999a). When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. Samples containing up to 61 preselected elements can be simultaneous analyzed by ICP at a rate of one sample per minute (US EPA, 1999a). In addition, the ICP technique has the ability to analyze a large range of concentrations. As with FAA and GFAA, the particulate matter must be extracted (via hot acid extraction or microwave extraction) and digested for ICP analysis, and the material introduced into the instrument is destroyed during analysis. An ICP instrument is more costly than many of the other instruments. The ICP detection limit for many of the elements of interest is equal to or somewhat better than most of the other instruments. High-volume samplers are typically used for sampling when ICP analysis is planned.

6.3.4 Inductively Coupled Plasma/Mass Spectroscopy

Other analytical methods such as Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) can be used to determine trace metal concentrations (Broekaert *et al.*, 1982; Janssen *et al.*, 1997). In ICP/MS analysis, the sample is excited using an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis allows many more than sixty elements and the isotopes of elements to be determined simultaneously at very low detection limits. However, ICP/MS analysis is time consuming because the sample must be extracted or digested and the analysis is destructive. In addition, the procedure is very costly and its documented applications are the lowest among all the potential techniques (US EPA, 1999a). Sampling is typically conducted using high-volume samplers when ICP/MS analysis is planned.

6.3.5 Proton Induced X-Ray Emission Spectroscopy

Some work on trace metal analysis has also been performed using Proton Induced X-Ray Emission (PIXE) Spectroscopy (Heidam, 1981; Van Borm *et al.*, 1990; Flores *et al.*, 1999). PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high-energy source, in this case high-energy protons, to remove inner shell electrons. Fluorescent X-ray photons are detected employing the same detection methods as XRF and used to identify and quantify different elements in the sample.

PIXE is one of the more commonly used elemental analysis methods because of its relatively low cost, nondestructive, multi-element capabilities. It is potentially capable of determining 72 elements with molecular weights between those of sodium and uranium, simultaneously (ARPEL, 1998). The method provides the sensitivity for accurate measurements at the nanogram or less level for many important trace metals in the urban atmosphere. The PIXE method has the ability to analyze a very small sample diameter in addition to evenly distributed wide-area samples, which is advantageous because it permits analysis of individual particle size fractions collected with single orifice type cascade impactors. PIXE is capable of measuring smaller quantities of particulate matter, although it has the same limitations as with XRF concerning light elements. In addition, facilities for this method are expensive and not common and it is less suitable for routine filter analysis than other multi-elemental methods because of more complicated sample preparation (US EPA, 1994). Analysis by PIXE typically involves collecting particulate matter by dichotomous or Partisol samplers.

6.3.6 Instrumental Neutron Activation Analysis Spectroscopy

Instrumental Neutron Activation Analysis (INAA) (Zoller and Gordon, 1970; Gladney *et al.*, 1974; Hopke *et al.*, 1976; Mizohata and Mamuro, 1979; Kowalczyk *et al.*, 1978, 1982; Olmez, 1989; Rizzio *et al.*, 1999; Salma and Zemplem-Papp, 1999) bombards a sample with a high neutron thermal flux in a nuclear reactor or accelerator. The sample elements are transformed into radioactive isotopes that emit gamma rays. The distribution or spectrum of energy of the gamma rays can be measured to determine the specific isotopes present. The intensity of the gamma rays can also be measured and is proportional to the amounts of elements present.

INAA is a simultaneous, multi-element method for determining ppt, ppm or ppb levels of 40-50 elements of interest. It has the advantage of higher sensitivity compared to other methods, a fact that makes it attractive for sampling trace elements found in extremely low concentrations (US EPA, 1999a). INAA is a non-destructive technique that requires minimal sample preparation as it does not require the addition of any foreign materials for irradiation. Limitations of this method include the fact that elements such as sulphur, lead and cadmium cannot be determined accurately, as well as that INAA is more expensive than many other methods. In addition, to use this method an optimal loading of >100 $\mu g/cm^2$ is generally required (Gordon et al, 1984). Analysis by INAA is compatible with sampling by high-volume, dichotomous and Partisol samplers.

6.3.7 Alternative Analytical Methods

There have been several reports of Energy Dispersive X-Ray (EDX) Spectrometry being used in conjunction with Scanning Electron Microscopy (SEM) (Linton *et al.*, 1980; Casuccio and Janocko, 1981; Shaw, 1983; Post and Buseck, 1984; Saucy *et al.*, 1987; Anderson *et al.*, 1988; Dzubay and Mamane, 1989; Hamilton *et al.*, 1994). Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) Spectrometry uses a computer-controlled scanning electron microscope equipped with image analysis software to determine the size and shape of a moderate number of particles and EDX to provide qualitative and a moderately sensitive quantitative elemental analysis in a similar manner as XRF analysis. Generally, low loadings are required to

employ this technique, therefore, a low-flow device such as dichotomous, Partisol or the MiniVol samplers should be used.

The primary advantage of the SEM-EDX technique is the ability to characterize individual particles both chemically and physically. The Expert Panel on the US Environmental Protection Agency $PM_{2.5}$ Chemical Speciation Network has recommended using the SEM-EDX for analysis of air filters (US EPA, 1999b). The panel found that microscopic techniques could be used to characterize both the morphology and the chemical composition of individual particles (Koutrakis, 1998). The disadvantages of the SEM-EDX technique include poor quantitative sensitivity (Linton *et al.*, 1980) and practical difficulties such as excessive time for a representative analysis and the occurrence of both particle damage and compositional changes during analysis (Post and Buseck, 1984). In addition, the EDX technique often results in potential spectral interferences requiring complex spectral deconvolution procedures.

Advances in microscopic techniques, particularly in sample analysis software, now permit collection of reasonably large datasets of individual particle morphology and composition. This technology has helped to overcome the sometimes-problematic issue of only being able to analyze a moderate number of particles in a reasonable time frame with the conventional SEM-EDX technique. To illustrate this point, an increasing number of studies in recent years (Rojas *et al.*, 1990; Van Borm *et al.*, 1989; Xhoffer *et al.*, 1991) have employed electron probe microanalysis to analyze individual particles. However, these technologies are very expensive, still in the developmental phase and are not readily available.

7.0 AMBIENT GUIDELINES

Current and/or recommended and proposed ambient guidelines of other jurisdictions in Canada, United States and elsewhere were reviewed for manganese. Details about guidelines that exist for each jurisdiction reviewed are presented in tabular format in Section 7.1. In general, all jurisdictions have common uses for their guidelines. These uses may include:

- reviewing permit applications for sources that emit air pollutants to the atmosphere,
- investigating accidental releases or community complaints about adverse air quality for the purpose of determining follow-up or enforcement activity,
- determining whether to implement temporary emission control actions under persistent adverse air quality conditions of a short-term nature

7.1 Manganese Air Quality Guidelines

Air quality guidelines for manganese are summarized in Table 10. The principal approaches by which guidelines are developed include:

- Using an occupational exposure level (OEL) and dividing it by safety or adjustment factors. The most common OEL used by most state agencies is the 8-hour threshold limit value (TLV) of 5,000 $\mu g/m^3$ for manganese dusts adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). The safety or adjustment factors are intended to account for issues such as: differences between eight-hour exposures in the workplace and continuous 24-hour environmental exposures, increased susceptibility of some people in the general population versus the relatively healthy worker, and uncertainty in the margin of safety provided in an occupational exposure limit.
- Using non-carcinogenic risk assessment procedures. A no observed adverse effect level (NOAEL) – or lowest observed adverse effect level (LOAEL) if a NOAEL is unavailable – from a suitable animal or human study is used. It is then divided by a series of adjustment factors. The adjustment factors are intended to account for issues such as: differences between animals and humans, sensitivity of high risk individuals, use of a LOAEL instead of a NOAEL, and for extrapolation from less-than-lifetime exposures to chronic exposure.

Table 10 Summary of Air Quality Guidelines for Manganese

Agency	Guideline Title	Guideline Value [µg/m³] Averaging Time:			
		1-hour	8-hour	24-hour	annual
Ontario MOE	Ambient Air Quality Criterion (AAQC):			2.5	
	Maximum point of impingement (POI) Guideline (30-min. averaging time):	7.5			
US ATSDR	Chronic inhalation Minimal Risk Level:				0.04
US EPA	Reference concentration (RfC):				0.05
California EPA	Chronic reference exposure level (REL):				0.2
Louisiana DEQ	Ambient air standard (AAS):		4.76		
Massachusetts DEP	No guideline exists.				
Michigan DEQ	Initial threshold screening level (ITSL):			0.05	
New Hampshire DES	24-hour ambient air limit (AAL):			1.006	
	Annual AAL:				0.05
New Jersey DEP	Risk assessment approach is used: Reference concentration (RfC):				0.05
North Carolina ENR	Acceptable ambient level (AAL):			0.031	
Ohio EPA	Maximum acceptable ground-level concentration (MAGLC):[a]	119			
Oklahoma DEQ	Maximum acceptable ambient concentration (MAAC):			100	
Rhode Island DEM	Acceptable ambient level (AAL):	2			
Texas CEQ	Effects screening level (ESL):	2			0.2
Vermont ANR	Hazardous ambient air standard (HAAS):				119
Washington DOE	Acceptable source impact level (ASIL):			0.4	
Wisconsin DNR	Ambient air concentration (AAC):[a]			4.8	
New Zealand MOE	No guideline exists.				
The Netherlands (RIVM)	No guideline exists.				
World Health Organization	Ambient air guidance value:				0.15

a Proposed.

Agency: Ontario Ministry of the Environment (OME).
Air Quality Guideline: Ambient Air Quality Criterion (AAQC) = 2.5 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Limiting effect based on health.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: Used by Ontario Ministry of Environment (OME) to represent human health or environmental effect-based values not expected to cause adverse effects based on continuous exposure.
Additional Comments: AAQC is not used by OME to permit stationary sources that emit manganese to the atmosphere. A "point of impingement" standard is used to for permitting situations.
Reference and Supporting Documentation: Ontario Ministry of the Environment. 1999. Summary of Point Of Impingement Standards, Point Of Impingement Guidelines, and Ambient Air Quality Criteria (AAQC). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. November 1999. 12 pp.

Agency: Ontario Ministry of the Environment (OME).
Air Quality Guideline: Maximum point of impingement (POI) Guideline = 7.5 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 30-minute averaging time.
Basis for Development: Limiting effect based on health.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: Used by OME to review permit applications for stationary sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Ontario Ministry of the Environment. 1999. Summary of Point Of Impingement Standards, Point Of Impingement Guidelines, and Ambient Air Quality Criteria (AAQC). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. November 1999. 12 pp.

Agency:

US Agency for Toxic Substances and Disease Registry (ATSDR).

Air Quality Guideline:

Chronic inhalation Minimal Risk Level (MRL) = 0.04 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

Greater than 365-day exposure duration.

Basis for Development:

The chronic inhalation MRL was derived using: (1) a NOAEL of 0.051 mg/m^3 for workers at a metal producing plant, (2) an uncertainty factor of 10 for human variability, (3) factors of 5/7 and 8/24 to account for intermittent exposure (5 days/week, 8 hours/day), (4) an uncertainty factor of 10 to account for limitations in the inhalation database, including the lack of data on developmental effects and data on the potential for reproductive effects in women, and the potential for differences in toxicity from different forms of manganese, and (5) a modifying factor of 5 for the potential for increased susceptibility in children based upon differences in the pharmacokinetic handling of manganese in young children.

Date Guideline Developed:

Unknown.

How Guideline is Used in Practice:

MRLs are intended to serve as a screening tool to help public health professionals decide where to look more closely. Chronic inhalation MRLs are exposure concentrations that based on current information, might cause adverse health effects in the people most sensitive to such substance-induced effects for 365 days, and longer, exposure durations.

Additional Comments:

Inhalation MRLs provide a basis for comparison with levels that people might encounter in air. If a person is exposed to manganese at an amount below the MRL, it is not expected that harmful (noncancer) health effects will occur. Because these levels are based only on information currently available, some uncertainty is always associated with them. Also, because the method for deriving MRLs does not use any information about cancer, an MRL does not imply anything about the presence, absence, or level of risk for cancer.

Reference and Supporting Documentation:

Agency for Toxic Substances and Disease Registry (ATSDR). 2003. Minimal Risk Levels (MRLs) for Hazardous Substances. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. Available at: http://www.atsdr.cdc.gov/mrls.html (accessed 22 January 2003).

Agency:

US Environmental Protection Agency (EPA).

Air Quality Guideline:

Reference concentration (RfC) = 0.05 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

Continuous exposure (daily exposure over a lifetime).

Basis for Development:

The RfC was developed as follows. A LOAEL was derived from an occupational-lifetime integrated respirable dust concentration of manganese dioxide (MnO_2) based on 8-hour time weighted average (TWA) occupational exposure multiplied by individual work histories in years (expressed as mg manganese (Mn)/m^3 x years). The geometric mean concentration (0.793 mg Mn)/m^3 years) was divided by the average duration of MnO_2 exposure (5.3 years) and adjustments were made to account for differences in mean daily respiratory air volumes between adults (20 m^3/day for continuous environmental exposure) versus adults in the workplace (10 m^3/day for occupational exposure) and 5 days occupational exposure versus 7 days continuous environmental exposure. The resulting adjusted LOAEL of 0.05 mg/m^3 was divided by uncertainty factors totaling 1000 to derive the RfC of 0.05 $\mu g/m^3$.

Date Guideline Developed:

1993.

How Guideline is Used in Practice:

The reference concentration (RfC) is intended for use by US EPA staff in risk assessments, decision-making and regulatory activities.

Additional Comments:

The Integrated Risk Information System (IRIS) is prepared and maintained by the US EPA. IRIS is an electronic database containing information on human health effects that may result from exposure to various chemicals in the environment.

Reference and Supporting Documentation:

US Environmental Protection Agency. Integrated Risk Information System. http://www.epa.gov/iris/ (accessed 22 January 2003).

Agency: California Environmental Protection Agency (Cal EPA).
Air Quality Guideline: Chronic reference exposure level (REL) = 0.2 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: Continuous (daily) exposure over a lifetime.
Basis for Development: The chronic REL represents a toxicity value recently adopted by Cal EPA Office of Environmental Health Hazard Assessment (OEHHA). The basis for development of the chronic REL is limited other then that it is based on nervous system effects.
Date Guideline Developed: 2000.
How Guideline is Used in Practice: Chronic RELs are for use in facility health risk assessments conducted for the AB 2588 Air Toxics "Hot Spots" Program.
Additional Comments: n/a
Reference and Supporting Documentation: California Environmental Protection Agency (Cal EPA). 1999. Determination of Acute Reference Exposure Levels for Airborne Toxicants. Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, Cal EPA. Oakland, CA. March 1999. California Office of Environmental Health Hazard Assessment (OEHHA)/Air Resources Board (ARB). 2001. Approved Chronic Reference Exposure Levels and Target Organs. Table 3 (last updated 13 September 2001). Available at: www.arb.ca.gov/toxics/healthval/chronic.pdf (accessed 22 January 2003).

Agency: Louisiana Department of Environmental Quality (DEQ).
Air Quality Guideline: Ambient air standard (AAS) for toxic air pollutants = 4.76 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 8-hour averaging time.
Basis for Development: Unknown.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: AASs are used by Louisiana DEQ to review permit applications for stationary sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: *Louisiana Administrative Code (LAC). Title 33 Environmental Quality, Part III Air, Chapter 51. Comprehensive Toxic Air Pollutant Emission Control Program. Louisiana Department of Environmental Quality. Baton Rouge, LA.*

Agency: Massachusetts Department of Environmental Protection (DEP).
Air Quality Guideline: Massachusetts DEP does not have an air quality guideline for manganese.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used in Practice: n/a
Additional Comments: n/a
Reference and Supporting Documentation: Massachusetts Department of Environmental Protection (DEP). 1995. Revised air guidelines [updated list of 24-hour average Threshold Effects Exposure Limit (TEL) values and annual average Allowable Ambient Limit (AAL) values]. Massachusetts DEP, Boston, MA. 6 December 1995. Memorandum available at: http://www.state.ma.us/dep/ors/files/aallist.pdf (accessed 22 January 2003).

Agency: Michigan Department of Environmental Quality (DEQ).
Air Quality Guideline: Initial threshold screening level (ITSL) = 0.05 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Based on US EPA's reference concentration of 0.05 $\mu g/m^3$.
Date Guideline Developed: 1993.
How Guideline is Used in Practice: There are two basic requirements of Michigan air toxic rules. First, each source must apply the best available control technology for toxics (T-BACT). After the application of T-BACT, the emissions of the toxic air contaminant cannot result in a maximum ambient concentration that exceeds the applicable health based screening level for non-carcinogenic effects (ITSL). Application of an ITSL is required for any new or modified emission source or sources for which a permit to install is requested and which emits a toxic air contaminant.
Additional Comments: The applicable air quality screening level for chemical treated as non-carcinogens by Michigan DEQ is the ITSL. There are two health based screening levels for chemical treated as carcinogens by Michigan DEQ: the initial risk screening level (IRSL) – based on an increased cancer risk of one in one million, and the secondary risk screening level (SRSL) – based on as an increased cancer risk of 1 in 100,000.
Reference and Supporting Documentation: *Michigan Administrative Code (MAC). Air Pollution Control Rules. Part 2 Air Use Approval. R 336.1201 - 336.1299. Air Quality Division, Department of Environmental Quality. Lansing, MI.*

Agency: New Hampshire Department of Environmental Services (DES).
Air Quality Guideline: 24-hour ambient air limit (AAL) = 1.006 $\mu g/m^3$. Annual ambient air limit (AAL) = 0.05 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: See above.
Basis for Development: The AALs were developed in the following manner: 24-hour Ambient Air Limit – Unknown. Annual Ambient Air Limit – The reference concentration (RfC) limit established by US EPA is used as the annual AAL.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: AALs are used by New Hampshire DES to review permit applications for sources that emit manganese to the atmosphere. Sources are regulated through a statewide air permitting system and include any new, modified or existing stationary source, area source or device.
Additional Comments: n/a
Reference and Supporting Documentation: *New Hampshire Administrative Rule. Chapter Env-A 1400. Regulated Toxic Air Pollutants. New Hampshire Department of Environmental Services. Concord, NH.*

Agency:

New Jersey Department of Environmental Protection (DEP).

Air Quality Guideline:

Applicants are required to carry out a risk assessment in conjunction with applying for an air pollution control pre-construction permit. In the case of manganese, the US Environmental Protection Agency RfC (2 $\mu g/m^3$) is used as the pollutant-specific reference concentration in which to calculate a Hazard Quotient for sources that emit manganese to the atmosphere.

Averaging Time To Which Guideline Applies:

Continuous exposure (daily exposure over a lifetime).

Basis for Development:

Based on US EPA's reference concentration (RfC) limit.

Date Guideline Developed:

December 1994.

How Guideline is Used in Practice:

n/a

Additional Comments:

n/a

Reference and Supporting Documentation:

New Jersey Administrative Code (NJAC). Title 7, Chapter 27, Subchapter 8. Permits and Certificates for Minor Facilities (and Major Facilities without an Operating Permit). New Jersey Department of Environmental Protection. Trenton, NJ.

New Jersey Department of Environmental Protection. 1994. Technical Manual 1003. Guidance on Preparing a Risk Assessment for Air Contaminant Emissions. Air Quality Permitting Program, Bureau of Air Quality Evaluation, New Jersey Department of Environmental Protection. Trenton, NJ. Revised December 1994.

Agency: North Carolina Department of Environment and Natural Resources (ENR).
Air Quality Guideline: Acceptable ambient level (AAL) = 0.031 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Not stated.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: A facility emitting manganese must limit its emissions so that the resulting modeled ambient levels at the property boundary remain below the health-based acceptable ambient level (AAL).
Additional Comments: n/a
Reference and Supporting Documentation: *North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2D.1100 – Air Pollution Control Requirements (Control of Toxic Air Pollutants). North Carolina Department of Environment and Natural Resources. Raleigh, NC.* *North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2Q.0700 – Air Quality Permit Procedures (Toxic Air Pollutant Procedures). North Carolina Department of Environment and Natural Resources. Raleigh, NC.*

Agency:

Ohio Environmental Protection Agency (EPA).

Air Quality Guideline:

Maximum acceptable ground-level concentration (MAGLC) = 119 $\mu g/m^3$ (proposed).

Averaging Time To Which Guideline Applies:

1-hour averaging time.

Basis for Development:

$$\text{MAGCL} = \frac{\text{TLV}}{10} \times \frac{8\,\text{hr}}{24\,\text{hr}} \times \frac{5\,\text{d}}{7\,\text{d}} = \frac{\text{TLV}}{42}.$$

The TLV is the ACGIH 8-hour time weighted average occupational exposure limit (OEL) of 5 mg/m^3 for manganese dusts. The TLV is adjusted by a safety factor of 10 to take into account greater susceptibility of the general population in comparison to healthy workers. The 8/24 and the 5/7 multipliers are used to relate the exposure to longer than 40-hour time periods and ascertain that the individual's total exposure will be no greater than that allowed by the TLV.

Date Guideline Developed:

January 1994 (proposed).

How Guideline is Used in Practice:

Used by Ohio EPA to review permit applications for sources that emit manganese to the atmosphere.

Additional Comments:

n/a

Reference and Supporting Documentation:

Ohio Environmental Protection Agency (EPA). 2003. Review of New Sources of Toxic Emissions. Air Toxics Unit, Division of Air Pollution Control, Ohio EPA. Columbus, OH. 11 pp (available at: http://www.epa.state.oh.us/dapc/atu/atu.html, accessed 22 January 2003).

Ohio Environmental Protection Agency (Ohio EPA). 1994. Review of New Sources of Air Toxic Emissions. Proposed for Public Comment. Division of Air Pollution Control, Ohio EPA. Columbus, OH. January 1994. 31 pp.

Agency: Oklahoma Department of Environmental Quality (DEQ).
Air Quality Guideline: Maximum acceptable ambient concentration (MAAC) = 100 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: The MAAC is the TLV for manganese dusts (ACGIH 8-hour time weighted average occupational exposure limit – OEL – of 5 mg/m^3) divided by a factor of 50. In this case, the factor of 50 is applied to substances that are considered by Oklahoma DEQ to be moderately toxic.
Date Guideline Developed: Not stated.
How Guideline is Used in Practice: MAACs are used by Oklahoma DEQ to review permit applications for sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: *Oklahoma Administrative Code (OAC). Title 252. Chapter 100. Air Pollution Control. 100:252-41 - Control of Emission of Hazardous and Toxic Air Contaminants. Oklahoma Department of Environmental Quality. Oklahoma City, OK.* Oklahoma Department of Environmental Quality (DEQ). 2002. Air Toxics Partial Listing [maximum acceptable ambient concentrations (MAAC) for air toxics]. Oklahoma City, OK. Available at: http://www.deq.state.ok.us/AQDNew/toxics/listings/pollutant_query_1.html (accessed 23 January 2003).

Agency: Rhode Island Department of Environmental Management (DEM).
Air Quality Guideline: Acceptable ambient level (AAL) = 2 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 1-hour averaging time.
Basis for Development: Not stated.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: AALs are used by Rhode Island DEM to review permit applications for sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: *Rhode Island Department of Environmental Management. 1992. Air Pollution Control Regulation No. 22. Division of Air and Hazardous Materials, Rhode Island Department of Environmental Management. Providence, RI. Amended 19 November 1992.*

Agency:

Texas Commission on Environmental Quality (CEQ) – formerly Texas Natural Resource Conservation Commission (TRNCC).

Air Quality Guideline:

Short-term effects screening level (ESL) = 2 $\mu g/m^3$.

Long-term effects screening level (ESL) = 0.2 $\mu g/m^3$.

Averaging Time To Which Guideline Applies:

1-hour averaging time for short-term ESL.

Annual averaging time for long-term ESL.

Basis for Development:

Short-term Effects Screening Level – unknown.

Long-term Effects Screening Level – unknown.

Date Guideline Developed:

Not stated.

How Guideline is Used in Practice:

ESLs are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in air. ESLs are based on data concerning health effects, odor nuisance potential, effects with respect to vegetation, and corrosion effects. They are not ambient air standards. If predicted or measured airborne levels of a chemical do not exceed the screening level, adverse health or welfare effects would not be expected to result. If ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review.

Additional Comments:

n/a

Reference and Supporting Documentation:

Texas Natural Resource Conservation Commission (TNRCC) 2001. Toxicology & Risk Assessment (TARA) Section Effects Screening Levels. http://www.tnrcc.state.tx.us/permitting/tox/index.html (accessed 23 January 2003).

Agency: Vermont Agency of Natural Resources (ANR).
Air Quality Guideline: Hazardous ambient air standard (HAAS) = 119 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: Annual average.
Basis for Development: Unknown, however the HAAS is equivalent to the TLV for manganese dusts (ACGIH 8-hour time weighted average occupational exposure limit – OEL – of 5 mg/m^3) divided by a factor of 42. The factor of 42 is a common adjustment representing a safety factor of 10 and 8/24 and 5/7 multipliers to convert 8-hour per 24-hour day and 5-day per 7-day week occupational exposures to continuous exposures.
Date Guideline Developed: Not stated.
How Guideline is Used in Practice: HAASs are used by Vermont ANR to review permit applications for stationary sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Vermont Air Pollution Control Regulations. 2001. State of Vermont Agency of Natural Resources. Air Pollution Control Division. Waterbury, VT. 29 November 2001. 187 pp.

Agency: Washington State Department of Ecology (DOE).
Air Quality Guideline: Acceptable source impact level (ASIL) = 0.4 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: ASILs are used by Washington State DOE to review permit applications for sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: *Washington Administrative Code (WAC). Chapter 173-460 WAC. Controls For New Sources Of Toxic Air Pollutants. Washington State Department of Ecology. Olympia, WA.*

Agency: Wisconsin Department of Natural Resources (DNR).
Air Quality Guideline: Ambient air concentration (AAC) = 4.8 $\mu g/m^3$ (proposed).
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown.
Date Guideline Developed: Not stated.
How Guideline is Used in Practice: AACs are used by Wisconsin DNR to review permit applications for sources that emit manganese to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: *Wisconsin Administrative Code (WAC). Air Pollution Control Rules. Chapter NR 445. Control of Hazardous Pollutants. Wisconsin Department of Natural Resources. Madison WI.*

Agency: New Zealand Ministry for the Environment (MOE) and New Zealand Ministry of Health (MOH).
Air Quality Guideline: New Zealand MOE and MOH do not have air quality criteria for manganese.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used in Practice: n/a
Additional Comments: n/a
Reference and Supporting Documentation: New Zealand Ministry for the Environment and Ministry of Health (New Zealand). 2000. Proposals for Revised and New Ambient Air Quality Guidelines. Discussion Document. Air Quality Technical Report No 16. Prepared by the Ministry for the Environment and the Ministry of Health. December 2000. 79 pp.

Agency: The Netherlands National Institute of Public Health and the Environment (RIVM)
Air Quality Guideline: RIVM does not have air quality criteria for manganese.
Averaging Time To Which Guideline Applies: n/a
Basis for Development: n/a
Date Guideline Developed: n/a
How Guideline is Used in Practice: n/a
Additional Comments: n/a
Reference and Supporting Documentation: The Netherlands National Institute of Public Health and the Environment (RIVM). 2001. Re-evaluation of human-toxicological maximum permissible risk levels. RIVN Report 711701 025. RIVN, Bilthoven, The Netherlands. March 2001. 297 pp.

Agency: World Health Organization (WHO)
Air Quality Guideline: Ambient air guidance value recommended for general population = 0.15 $\mu g/m^3$.
Averaging Time To Which Guideline Applies: Annual average.
Basis for Development: The guideline value was based on neurotoxic effects observed in occupationally exposed workers and derived using the benchmark approach by WHO (2000). An estimated NOAEL of 30 $\mu g/m^3$ was dividing by a factor of 4.2 to adjust for continuous exposure and an uncertainty factor of 50 (10 for interindividual variation and 5 for developmental effects in younger children).
Date Guideline Developed: 2000.
How Guideline is Used in Practice: The guideline is intended to provide background information and guidance to governments in making risk management decisions, particularly in setting standards.
Additional Comments: n/a
Reference and Supporting Documentation: World Health Organization (WHO). 2000. Air Quality Guidelines for Europe, 2nd Edition. WHO Regional Publications, European Series, No. 91. WHO Regional Office for Europe, Copenhagen. 273 pp

7.1.1 Canada

The Ontario Ministry of the Environment (MOE) adopted an Ambient Air Quality Criterion (AAQC) of 2.5 $\mu g/m^3$ as a 24-hour guideline. Ontario MOE uses a maximum point of impingement (POI) guideline of 7.5 $\mu g/m^3$ based on a 30-minute averaging time to review permit applications for stationary sources that emit manganese to the atmosphere.

7.1.2 United States

The US Agency for Toxic Substances and Disease Registry (ATSDR) adopted a minimal risk level (MRL) of 0.04 $\mu g/m^3$ and the US Environmental Protection Agency (EPA) has a reference concentration (RfC) of 0.05 $\mu g/m^3$ for manganese. Michigan, New Hampshire, and New Jersey were states that adopted the US EPA RfC for their guidelines with corresponding averaging times ranging from 24 hours to greater than one year. Ohio, Oklahoma, and Vermont were states that adopted guidelines with averaging times ranging from 1-hour to greater than one-year based on the American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of 5 mg/m^3 for manganese dusts.

7.1.3 International Agencies

The New Zealand Ministry of Environment and Ministry of Health and the Netherlands National Institute of Public Health (RIVM, 2001) do not have air quality criteria for manganese. The World Health Organization (WHO, 2000) recently adopted an ambient air guidance value of 0.15 $\mu g/m^3$ as an annual average for manganese.

8.0 RISK CHARACTERIZATION

Risk characterization of an ambient air contaminant involves the integration and evaluation of several types of key information. Where it is undertaken for a site-specific situation, such as for the screening assessment of proposed industrial emissions of manganese, quantitative approaches can be used. For ambient air exposures, this may involve taking measurements or using a computer dispersion model to estimate ambient ground-level concentrations of manganese under different averaging times and making comparisons to safe levels of exposure (air quality guidelines).

For the general case, however, use of site-specific risk characterization approaches is limited unless a number of assumptions are made. The emission characteristics for sources of manganese release to air in Alberta vary for point sources such as industrial emissions. In addition, meteorological dispersion conditions can vary from site to site. This variability is difficult to represent as a general case for quantitative assessment and the resulting risk characterization would have substantial uncertainty. As a result, a qualitative risk characterization approach is used to evaluate issues associated with manganese in ambient air. The types of key information evaluated can include, but not be limited to:

- relevant chemical forms in air
- pathways by which exposure may occur
- relevant potential effects (impacts)

These issues are discussed further below.

8.1 Relevant Chemical Forms

Elemental manganese and inorganic manganese compounds have negligible vapour pressures but may exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils. Manganese- containing particles are mainly removed from the atmosphere by gravitational settling, with large particles tending to fall out faster than small particles.

8.2 Exposure Assessment

In considering the potential for inhalation exposure for humans, background levels of manganese in community ambient air tend to be low. Greater variability in ambient levels of manganese is expected near industrial point sources.

8.3 Toxicity Assessment

Breathing too much manganese dust over a short or long time can cause irritation of the lungs. Sometimes this makes breathing difficult, and it can also increase the chances of getting a lung infection, such as pneumonia. However, this can happen from breathing in many kinds of dust

particles and not just those that contain manganese. The primary health effects endpoints associated with inhalation of inorganic manganese compounds in humans are neurotoxicity, reproductive dysfunction, and impaired respiratory system (due to particulate exposures). Most significant to human exposures are the neurological effects associated with chronic inhalation exposures. These endpoints have been observed in the workplace.

8.4 Characterization of Risk

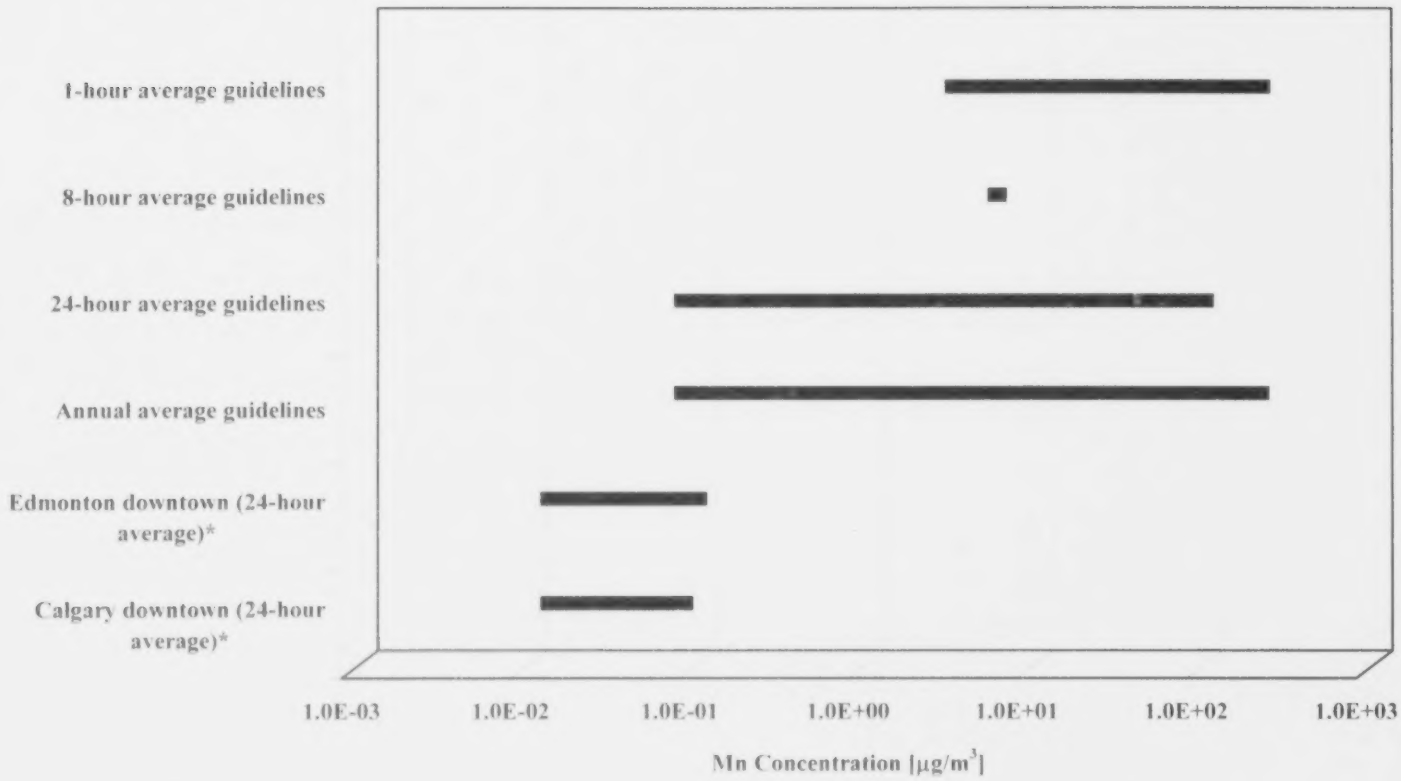
With respect to protection of the general population from inhalation exposure to manganese and other air toxics released from industrial activities, acute (short-term) exposure situations tend only to receive attention from regulatory agencies during the permitting process. An example of this is the use of computer dispersion models to estimate ambient ground-level concentrations of air toxics emitted from an industry under short-term (e.g. hourly) averaging times and making comparisons to air quality criteria with similar averaging times to meet agency permitting requirements. The occurrences of elevated levels of air toxics in the environment are in general, short-term and probably a result of stagnant meteorological conditions (poor dispersion of air) or accidental releases from industry.

However, a common approach used by regulatory agencies to protect the general population from exposure to potentially toxic chemicals in the environment is through the development and use of media guidelines for chronic (long-term) exposure conditions. For example, this is evident in Canada with how potentially toxic chemicals are addressed in the Guidelines for Canadian Drinking Water Quality for drinking water protection (Health Canada, 2001b) and Canadian Environmental Quality Guidelines for soil quality protection (CCME, 1999).

With respect to chronic (long-term) exposure conditions, neurological effects represent a health effects endpoint of interest to regulatory agencies. The ability for low ambient levels of inorganic manganese (i.e. $<<1$ $\mu g/m^3$) to contribute to neurological effects in the general population is uncertain. As a result, some regulatory agencies adopt air quality guidelines for manganese in order to protect humans.

The range of air quality guidelines proposed by various agencies for protection of human receptors is shown in Figure 1 for different averaging time periods. The data presented in Figure 1 were summarized from the previous section. Also shown in this Figure is the range between the median and maximum 24-hour average concentration of manganese in respirable particulate matter ($PM_{2.5}$) from air samples collected in central Edmonton and central Calgary from June 1991 to November 2000 (after AENV, 2003).

Urban settings – in which most air quality data are available for – are settings with higher metal concentrations in ambient air compared to rural settings (WHO, 2000). Figure 1 illustrates that the range between the median and maximum 24-hour average concentration of manganese in $PM_{2.5}$ tends to be on the low side and less than air quality guidelines for protection of human receptors (irrespective of averaging time).



* Range between the median and maximum 24-hour average concentration of manganese in airborne PM2.5

Figure 1 Range of Air Quality Guidelines for Manganese Proposed by Various Agencies for Protection of Human Receptors

9.0 REFERENCES

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APPENDIX A

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
2537	Safety-Kleen Ltd.	Corunna	ON	0.001	0.000	457.400	0.000	457.401
1036	Sheerness Generating Station	Hanna	AB	0.000	0.000	305.908	0.000	305.908
3649	Ispat Sidbec Inc.	Contrecoeur	QC	6.350	0.000	288.820	0.000	295.170
2284	TransAlta Corporation	Duffield	AB	3.217	0.000	208.356	0.000	211.573
0606	Esco Limited	Port Coquitlam	BC	4.570	0.000	196.190	0.000	200.760
5871	St Marys Cement Company	St Marys	ON	50.680	0.000	127.080	0.000	177.760
1651	Gerdau MRM Steel Inc.	Selkirk	MB	2.030	0.041	167.517	0.000	169.588
4000	Nova Scotia Power Inc.	Point Aconi	NS	0.000	0.000	135.700	0.000	135.700
3824	Co-Steel Lasco	Whitby	ON	0.020	0.116	132.000	0.000	132.136
5859	St. Marys Paper Ltd.	Sault Ste. Marie	ON	0.000	126.000	0.000	0.000	126.000
1383	Pope & Talbot Ltd.	Nanaimo	BC	0.115	35.436	79.760	0.000	115.311
3242	La Compagnie Abitibi-Consolidated du Canada	St-Félicien	QC	0.000	38.000	71.000	0.000	109.000
1861	Ontario Power Generation Inc	Nanticoke	ON	0.785	0.310	106.537	0.000	107.632
5460	Wabush Mines	Wabush	NL	100.300	0.000	0.000	0.000	100.300
2286	TransAlta Corporation	Duffield	AB	1.077	0.000	93.284	0.000	94.361
2181	St. Anne-Nackawic Company Ltd.	Nackawic	NB	0.074	58.739	33.096	0.000	91.909
0723	Norske Skog Canada Limited	Powell River	BC	0.070	90.060	0.000	0.000	90.130
2001	Compagnie Abitibi Consolidated Canada	Baie-Comeau	QC	0.053	26.280	58.883	0.000	85.216
2219	Smurfit-Stone Container (Canada) Inc.	Bathurst	NB	0.054	0.014	83.600	0.000	83.668
1419	Howe Sound Pulp and Paper Limited Partnership	Port Mellon	BC	0.066	23.068	53.369	0.000	76.503
2604	Irving Pulp & Paper Limited / Irving Tissue Company	Saint John	NB	0.120	26.590	45.560	0.000	72.270
3185	Domtar Inc.	Espanola	ON	0.025	32.218	39.412	0.000	71.655
1797	Canadian Forest Products Ltd.	Prince George	BC	1.913	33.689	35.804	0.000	71.406
0271	Emballages Smurfit-Stone Canada inc	Portage-du-Fort	QC	0.050	18.180	48.590	0.000	66.820
4063	Canfor	Prince George	BC	0.041	28.800	34.300	0.000	63.141
2948	Tembec Inc	Témiscaming	QC	0.028	12.034	50.113	0.000	62.175

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
2282	TransAlta Corporation	Wabamun	AB	0.852	0.000	61.183	0.000	62.035
1809	Ontario Power Generation Inc	Courtright	ON	0.156	0.015	61.493	0.000	61.664
5008	AV Cell Inc.	Atholville	NB	0.208	36.960	18.660	0.000	55.828
2872	Western Pulp Limited Partnership	Squamish	BC	0.000	0.000	51.640	0.000	51.640
1106	AltaSteel Ltd.	Edmonton	AB	2.661	0.011	48.050	0.000	50.722
0928	Weyerhaeuser Company Limited	Dryden	ON	0.597	25.780	19.363	0.000	45.740
3610	Weyerhaeuser Saskatchewan Limited	Prince Albert	SK	0.130	18.585	26.771	0.000	45.486
5105	Abitibi Consolidated Company of Canada	Mackenzie	BC	0.052	1.340	43.450	0.000	44.842
2875	Weyerhaeuser Company Ltd.	Grande Prairie	AB	0.142	13.191	31.164	0.000	44.497
3996	Nova Scotia Power Inc.	Trenton	NS	0.000	0.000	41.300	0.000	41.300
2158	Skeena Cellulose Inc.	Port Edward	BC	0.712	12.900	26.000	0.000	39.612
2991	Weldwood of Canada	Hinton	AB	0.679	14.601	23.906	0.000	39.186
5459	Mines Wabush	Sept-Iles	QC	1.280	37.500	0.000	0.000	38.780
3571	Ville de Montréal	Montréal	QC	0.014	38.424	0.000	0.000	38.438
3992	Nova Scotia Power Inc.	New Waterford	NS	0.000	0.000	38.400	0.000	38.400
3140	Emballages Smurfit-Stone Canada inc.	La Tuque	QC	0.024	36.626	0.000	0.000	36.650
3394	Irving Paper	Saint John	NB	0.010	33.450	0.000	0.000	33.460
1486	Pope & Talbot Ltd.	Mackenzie	BC	0.030	15.250	16.650	0.000	31.930
2924	Weyerhaeuser Company Limited	Kamloops	BC	1.114	30.630	0.000	0.000	31.744
0479	Cariboo Pulp and Paper Co.	Quesnel	BC	0.990	27.200	2.760	0.000	30.950
1195	Papier de Communication Domtar	Windsor	QC	0.334	0.241	27.760	0.000	28.335
0983	Abitibi-Consolidated du Canada	Alma	QC	0.166	1.246	26.051	0.000	27.463
1708	New Brunswick Power	New Castle Creek	NB	0.078	0.000	27.145	0.000	27.223
1266	Norske Skog Canada Limited	Crofton	BC	0.070	25.320	1.446	0.000	26.836
1185	Tembec Industries Inc.	Cranbrook	BC	0.000	7.700	17.752	0.000	25.452
1528	Papiers Fraser inc.	Thurso	QC	0.446	11.527	12.341	0.000	24.314

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
5246	Gerdau Mrm Steel Inc.	Selkirk	MB	1.809	0.000	21.627	0.000	23.436
2377	Western Pulp Limited Partnership	Port Alice	BC	0.155	18.064	4.131	0.000	22.350
0004	Tembec Industries	Pine Falls	MB	4.857	1.493	12.532	0.000	18.882
0333	NorskeCanada	Campbell River	BC	0.090	18.760	0.000	0.000	18.850
5283	Russel Metals Inc.	Edmonton	AB	0.000	0.000	17.000	0.000	17.000
0223	Daishowa-Marubeni International	MD of Northern Lights	AB	1.559	4.860	10.020	0.000	16.439
5710	Canadian Drawn Steel Company Inc.	Hamilton	ON	0.000	0.000	15.900	0.000	15.900
2051	Tolko Manitoba Kraft Papers	The Pas	MB	0.379	5.956	8.462	0.000	14.797
1465	Inco Limited	Copper Cliff	ON	0.000	13.675	0.000	0.000	13.675
5970	City of Hamilton	Hamilton	ON	0.000	13.466	0.000	0.000	13.466
0001	Alberta Pacific Forest Industries Inc.	Boyle	AB	0.000	0.720	12.240	0.000	12.960
0978	Abitibi Consolidated Company of Canada	Iroquois Falls	ON	0.030	3.276	9.648	0.000	12.954
0929	Bowater Produits Forestiers du Canada Inc.	Gatineau	QC	0.200	12.680	0.000	0.000	12.880
3171	Eurocan Pulp and Paper Company	Kitimat	BC	0.270	0.000	12.380	0.000	12.650
2587	Abitibi Consolidated Du Canada	Grand-Mère	QC	0.201	8.836	3.536	0.000	12.573
1338	Greater Vancouver Regional District	Delta	BC	0.000	11.860	0.000	0.000	11.860
0462	Marathon Pulp Inc.	Marathon	ON	0.034	10.947	0.000	0.000	10.981
4317	Lafarge Canada Inc.	Brookfield	NS	0.000	0.000	10.863	0.000	10.863
5009	Abitibi-Consolidated Inc.	Grand Falls-Windsor	NL	0.018	9.812	0.777	0.000	10.607
5189	Greater Vancouver Regional District	Richmond	BC	0.000	10.540	0.000	0.000	10.540
5841	St Marys Cement Company	Bowmanville	ON	0.110	0.000	10.390	0.000	10.500
1197	Domtar Papers	Cornwall	ON	0.676	9.120	0.000	0.000	9.796
1221	Nexfor Fraser Papers Inc.	Edmundston	NB	0.381	8.830	0.000	0.000	9.211
5527	Bowater inc.	Donnacona	QC	0.005	8.971	0.000	0.000	8.976
2984	Stelco Inc.	Hamilton	ON	7.255	0.000	0.000	0.000	7.255
0770	City of Ottawa	Ottawa	ON	0.000	7.000	0.000	0.000	7.000

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
1561	Kronos Canada, inc.	Varennes	QC	0.000	6.530	0.000	0.000	6.530
4806	Qit-Fer Et Titane Inc.	Sorel-Tracy	QC	6.244	0.000	0.000	0.000	6.244
5390	City of Edmonton	Edmonton	AB	0.000	6.140	0.000	0.000	6.140
3828	Compagnie Abitibi-Consolidated du Canada	Amos	QC	0.000	1.536	3.862	0.000	5.398
5850	Lafarge Canada Inc.	Bath	ON	0.108	0.000	4.656	0.000	4.764
2173	Spruce Falls Inc.	Kapuskasing / District of Coch	ON	0.033	4.283	0.000	0.000	4.316
7170	Voyageur Panel	Barwick	ON	4.090	0.000	0.000	0.000	4.090
1593	Norske Skog Canada Limited	Port Alberni	BC	0.133	3.751	0.000	0.000	3.884
1070	Algoma Steel Inc	Sault Ste. Marie	ON	0.240	3.559	0.000	0.000	3.799
3416	Ford Motor Company	Windsor	ON	2.200	1.500	0.000	0.000	3.700
1525	Papier Masson Limitée	Masson-Angers	QC	0.004	3.490	0.000	0.000	3.494
3048	Ontario Power Generation Inc	Thunder Bay	ON	0.077	0.000	2.993	0.000	3.070
4803	La Compagnie Abitibi-Consolidated Du Canada	Clermont	QC	0.029	2.989	0.000	0.000	3.018
3713	Dofasco Inc.	Hamilton	ON	2.420	0.290	0.000	0.000	2.710
1547	Metal Technologies-Woodstock Ltd.	Woodstock	ON	2.401	0.000	0.000	0.000	2.401
1520	Ivaco Rolling Mills Limited Partnership	L'Orignal	ON	2.003	0.000	0.000	0.000	2.003
2815	Falconbridge Ltd-Kidd Metallurgical Div.	Timmins/District of Cochrane	ON	0.064	1.822	0.000	0.000	1.886
3197	Williams Operating Corporation	Marathon	ON	0.183	1.684	0.000	0.000	1.867
0444	Inco Limited	Copper Cliff	ON	1.747	0.000	0.000	0.000	1.747
1236	Falconbridge Limited	Falconbridge	ON	1.665	0.028	0.001	0.000	1.694
2986	Stelco McMaster Ltée	Contrecoeur	QC	1.680	0.000	0.000	0.000	1.680
7107	Ks Centoco Wheel Corporation	Tilbury	ON	1.489	0.000	0.000	0.000	1.489
7096	Archie McCoy Hamilton Ltd	Troy	ON	1.299	0.000	0.000	0.000	1.299
3623	Noranda Inc	Rouyn-Noranda	QC	0.292	0.815	0.000	0.000	1.107
1656	Motor Coach Industries Limited	Winnipeg	MB	1.050	0.000	0.000	0.000	1.050

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
5740	Harvard Industries, Inc.	Dundalk	ON	1.001	0.000	0.000	0.000	1.001
4537	F & P Mfg., Inc.	Tottenham	ON	0.000	0.000	0.000	0.000	0.956
3855	Lake Erie Steel Company	Nanticoke	ON	0.834	0.053	0.000	0.000	0.887
7113	Volvo Motor Graders	Goderich	ON	0.000	0.000	0.000	0.000	0.847
4169	Gerdau Steel Inc.	Cambridge	ON	0.770	0.000	0.000	0.000	0.770
2380	Westcast Industries Inc.	Wingham	ON	0.738	0.000	0.000	0.000	0.738
5812	Dana - Brake Parts Canada Inc.	St. Catharines	ON	0.681	0.000	0.000	0.000	0.681
4993	TrentonWorks Ltd.	Trenton	NS	0.680	0.000	0.000	0.000	0.680
2161	Slater Steels Inc.	Hamilton	ON	0.661	0.000	0.000	0.000	0.661
4419	Timminco Limited	Haley	ON	0.000	0.000	0.000	0.000	0.614
5668	Brake Parts Sudbury	Sudbury	ON	0.614	0.000	0.000	0.000	0.614
0267	Edmonton Power Inc.	Warburg	AB	0.593	0.000	0.000	0.000	0.593
1394	Heckett MultiServ Canada	Nanticoke	ON	0.000	0.000	0.000	0.000	0.563
4048	Consumers' Co-operative Refineries Ltd./NewGrade Energy Inc.	Regina	SK	0.557	0.000	0.000	0.000	0.557
7040	Wescast Industries Inc.	Wingham	ON	0.546	0.000	0.000	0.000	0.546
3875	Cascades Inc.	East Angus	QC	0.500	0.000	0.000	0.000	0.500
5665	Dana Canada Inc.	Thorold	ON	0.500	0.000	0.000	0.000	0.500
3928	Ultramar Ltée	St-Romuald	QC	0.046	0.414	0.000	0.000	0.460
5600	Babcock & Wilcox Canada	Cambridge	ON	0.000	0.000	0.000	0.000	0.458
5516	Louisiana-Pacific Canada Ltd	St-Michel-des-Saints	QC	0.423	0.000	0.000	0.000	0.423
2381	Wescast Industries Inc.	Brantford	ON	0.421	0.000	0.000	0.000	0.421
3802	Teck Cominco Metals Limited	Trail	BC	0.010	0.400	0.000	0.000	0.410
4796	Les Aciers Canam	St-Gedeon	QC	0.400	0.000	0.000	0.000	0.400
5910	Wabi Iron & Steel Corp.	New Liskeard	ON	0.392	0.000	0.000	0.000	0.392
7072	Energy Plus 2000 Limited	Ajax	ON	0.000	0.000	0.000	0.000	0.310
5313	Foothills Steel Foundry Ltd.	Calgary	AB	0.000	0.000	0.000	0.000	0.300

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
1388	Heckett MultiServ Canada	Hamilton	ON	0.000	0.000	0.000	0.000	0.298
1391	Heckett MultiServ Canada	Hamilton	ON	0.000	0.000	0.000	0.000	0.282
5945	Alltech Inc.	Alexandria	ON	0.273	0.000	0.000	0.000	0.273
5672	Tenneco Automotive	Cambridge	ON	0.000	0.000	0.000	0.000	0.271
1397	Heckett MultiServ Canada	Contrecoeur	QC	0.000	0.000	0.000	0.000	0.257
5704	TML Industries Ltd.	Pickering	ON	0.000	0.000	0.000	0.000	0.250
5949	Cosma International	St. Catharines	ON	0.237	0.000	0.000	0.000	0.237
5129	VAE Nortrak Ltd	Richmond	BC	0.000	0.000	0.235	0.000	0.235
2683	Presstran Industries	St Thomas	ON	0.000	0.000	0.000	0.000	0.232
3883	Ford Motor Company	St. Thomas	ON	0.002	0.230	0.000	0.000	0.232
4705	Rapistan Systems	Mississauga	ON	0.231	0.000	0.000	0.000	0.231
3158	Slater Stainless Corp.	Welland	ON	0.165	0.052	0.000	0.000	0.217
4912	TKA Fabco Corp	Dresden	ON	0.201	0.008	0.000	0.000	0.209
1224	Sterling, A Division of Freightliner Limited	St. Thomas	ON	0.000	0.000	0.000	0.000	0.206
4907	Budd Canada Inc.	Kitchener	ON	0.205	0.000	0.000	0.000	0.205
4637	Tka Fabco Corp	Windsor	ON	0.182	0.021	0.000	0.000	0.203
0851	CP Loewen Enterprises	Steinbach	MB	0.200	0.000	0.000	0.000	0.200
0315	ESCO Limited	Port Hope	ON	0.056	0.000	0.141	0.000	0.197
0057	Bombardier Transport	La Pocatière	QC	0.183	0.000	0.000	0.000	0.183
2496	Amcan Castings Limited	Hamilton	ON	0.000	0.000	0.000	0.000	0.181
3152	Oxford Automotive Canada Ltd.	Wallaceburg	ON	0.176	0.000	0.000	0.000	0.176
0455	Ingot Metal Company Limited	Weston	ON	0.000	0.000	0.000	0.000	0.170
4797	Les Forges de Sorel Inc.	St-Joseph-de-Sorel	QC	0.162	0.000	0.000	0.000	0.162
1344	Griffin Canada Inc.	Winnipeg	MB	0.070	0.000	0.090	0.000	0.160
5253	Cutler-Hammer	Airdrie	AB	0.160	0.000	0.000	0.000	0.160
4539	Standard Induction Castings Inc.	Windsor	ON	0.155	0.000	0.000	0.000	0.155

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
3704	Imperial Oil	Sarnia	ON	0.134	0.000	0.000	0.000	0.134
0711	Flint Ink North America Corporation	Concord	ON	0.000	0.000	0.000	0.000	0.131
7001	Robertson Building Systems Ltd	Hamilton	ON	0.129	0.000	0.000	0.000	0.129
7150	Techform Products Limited	Penetanguishene	ON	0.000	0.000	0.000	0.000	0.126
5760	AECON Industrial	Cambridge	ON	0.124	0.000	0.000	0.000	0.124
0796	Corus S.E.C.	Cap-de-la-Madeleine	QC	0.120	0.000	0.000	0.000	0.120
5276	Flexi-Coil	Saskatoon	SK	0.000	0.000	0.000	0.000	0.120
1698	New Brunswick Power	Belledune	NB	0.117	0.000	0.000	0.000	0.117
5723	Unimotion Gear	Aurora	ON	0.000	0.000	0.000	0.000	0.117
4819	Norcast Castings company	Mont-Joli	QC	0.099	0.015	0.000	0.000	0.114
2446	I-XL Industries Ltd.	Medicine Hat	AB	0.000	0.000	0.104	0.000	0.104
5745	Westcast Industries	Stratford	ON	0.104	0.000	0.000	0.000	0.104
0870	Q3 Aluminum Technologies Inc.	Long-Sault	ON	0.100	0.000	0.000	0.000	0.100
1770	Kirkland Lake Power Corp.	Kirkland Lake	ON	0.100	0.000	0.000	0.000	0.100
1773	Cochrane Power Corp.	Cochrane	ON	0.100	0.000	0.000	0.000	0.100
2844	Ontario Power Generation Inc.	Mississauga	ON	0.098	0.002	0.000	0.000	0.100
3901	Petro-Canada	Oakville	ON	0.013	0.000	0.087	0.000	0.100
4785	Canam Steel Works	Mississauga	ON	0.100	0.000	0.000	0.000	0.100
4801	Manac	St-Georges	QC	0.100	0.000	0.000	0.000	0.100
5732	Wabash Alloys	Mississauga	ON	0.098	0.000	0.000	0.000	0.098
0701	Kubota Metal Corporation	Orillia	ON	0.097	0.000	0.000	0.000	0.097
5800	Fileco Inc.	Concord	ON	0.091	0.000	0.000	0.000	0.091
3953	Slater Stainless Corp.	Sorel-Tracy	QC	0.080	0.010	0.000	0.000	0.090
3453	Meritor Suspension Systems Company	Milton	ON	0.069	0.000	0.000	0.000	0.069
7039	KTH Shelburne MFG., Inc.	Shelburne	ON	0.000	0.000	0.000	0.000	0.069
3395	Les Poudres Metalliques du Quebec Ltee	Sorel-Tracy	QC	0.000	0.000	0.000	0.000	0.068

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
5682	Russel Metals Inc	Calgary	AB	0.066	0.000	0.000	0.000	0.066
4716	Hobart Brothers Of Canada - An ITW Canada Company	Woodstock	ON	0.000	0.000	0.000	0.000	0.065
4546	Stanley Canada Inc	Smiths Falls	ON	0.063	0.000	0.000	0.000	0.063
2312	Tuyaux Wolverine (Canada) inc.	Montréal-Est	QC	0.060	0.000	0.000	0.000	0.060
5738	Thomas Built Buses Inc.	Woodstock	ON	0.060	0.000	0.000	0.000	0.060
5835	Timberjack, Inc	Woodstock	ON	0.060	0.000	0.000	0.000	0.060
3701	Imperial Oil Limited	Nanticoke	ON	0.057	0.000	0.000	0.000	0.057
0280	Dow Chemical Canada Incorporated	Fort Saskatchewan	AB	0.000	0.000	0.000	0.053	0.053
3149	Oxford Automotive Canda Ltd.	Chatham	ON	0.053	0.000	0.000	0.000	0.053
1269	Nemak of Canada Corporation	Windsor	ON	0.050	0.000	0.000	0.000	0.050
3707	Imperial Oil	Edmonton	AB	0.050	0.000	0.000	0.000	0.050
7108	COLUMBUS Mckinnon LIMITED.	COBOURG	ON	0.050	0.000	0.000	0.000	0.050
2570	Cam-Slide Mfg. I	Newmarket	ON	0.000	0.000	0.000	0.000	0.048
3227	General Motors of Canada Limited	St. Catharines	ON	0.023	0.023	0.000	0.000	0.046
5897	Durham Furniture Inc.	Durham	ON	0.000	0.000	0.000	0.000	0.046
2636	Compagnie Abitibi-Consolidated du Canada	La Baie	QC	0.045	0.000	0.000	0.000	0.045
7081	Proboard Ltd.	Atikokan	ON	0.000	0.000	0.000	0.000	0.045
4447	Skyjack Inc.	Guelph	ON	0.000	0.000	0.000	0.000	0.043
1951	Chemfil Canada Ltd	Windsor	ON	0.000	0.000	0.000	0.000	0.039
4980	Zalev Brothers Co.	Windsor	ON	0.030	0.005	0.000	0.000	0.035
7083	Bernardo Metal Products Ltd.	Mississauga	ON	0.035	0.000	0.000	0.000	0.035
5606	Multichair Inc.	Mississauga	ON	0.034	0.000	0.000	0.000	0.034
7134	North American Tillage Tools Company	Hamilton	ON	0.032	0.000	0.000	0.000	0.032
3403	Stelpipe Ltd.	Welland	ON	0.000	0.030	0.000	0.000	0.030
4781	Ford of Canada	Windsor/Essex	ON	0.030	0.000	0.000	0.000	0.030
5918	Multichair Inc.	Mississauga	ON	0.030	0.000	0.000	0.000	0.030

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
2182	St.Lawrence Cement	Mississauga	ON	0.029	0.000	0.000	0.000	0.029
4472	Wabtec Foundry Limited	Wallaceburg	ON	0.026	0.000	0.000	0.000	0.026
2209	Welland Pipe Ltd.	Welland	ON	0.000	0.000	0.000	0.000	0.025
7145	Dresden Industrial	St. Mary's	ON	0.025	0.000	0.000	0.000	0.025
3430	Degussa Canada Inc.	Brampton	ON	0.000	0.000	0.000	0.000	0.024
5896	SKD Company	Brampton	ON	0.023	0.000	0.000	0.000	0.023
4987	ROR Industries Inc.	Moncton	NB	0.022	0.000	0.000	0.000	0.022
2499	Microprecision Die Casting Inc.	Burlington	ON	0.000	0.000	0.000	0.000	0.021
5844	Oxford Automotive Products	Cambridge	ON	0.021	0.000	0.000	0.000	0.021
5636	Babcock & Wilcox Canada	Melville	SK	0.000	0.000	0.000	0.000	0.020
7046	Crane Plumbing Corporation	Stratford	ON	0.019	0.000	0.000	0.000	0.019
3905	Petro-Canada	Port Moody	BC	0.000	0.018	0.000	0.000	0.018
4737	Dana Canada Inc.	Barrie	ON	0.018	0.000	0.000	0.000	0.018
5939	Hidden Hitch of Canada	Huntsville	ON	0.017	0.000	0.000	0.000	0.017
2687	Deco Automotive	Rexdale	ON	0.000	0.000	0.000	0.000	0.015
4601	Anchor Lamina Inc.	Windsor	ON	0.015	0.000	0.000	0.000	0.015
5630	Mytox	Woodbridge	ON	0.000	0.000	0.000	0.000	0.015
1712	New Brunswick Power	Dalhousie	NB	0.014	0.000	0.000	0.000	0.014
0117	ArvinMeritor Commercial Vehicle Systems	Toronto	ON	0.013	0.000	0.000	0.000	0.013
2677	P&F Tool and Die	Concord	ON	0.000	0.000	0.000	0.000	0.013
3870	General Motors of Canada Limited	Oshawa	ON	0.013	0.000	0.000	0.000	0.013
4205	A.H. Tallman Bronze Co. Ltd.	Burlington	ON	0.013	0.000	0.000	0.000	0.013
5474	Lafarge Canada inc.	Saint-Constant	QC	0.013	0.000	0.000	0.000	0.013
5663	Bombardier Transportation	Millhaven	ON	0.013	0.000	0.000	0.000	0.013
5967	Kromet International Inc.	Cambridge	ON	0.013	0.000	0.000	0.000	0.013
7042	Formet East	Rexdale	ON	0.013	0.000	0.000	0.000	0.013

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
7158	Titan Tool & Die	Windsor	ON	0.013	0.000	0.000	0.000	0.013
5153	Lafarge Canada Inc.	Kamloops	BC	0.012	0.000	0.000	0.000	0.012
5469	International Comfort Products division of UTC Canada	Sherbrooke	QC	0.012	0.000	0.000	0.000	0.012
5917	Anotech	Concord	ON	0.000	0.000	0.000	0.000	0.012
1534	John Deere Limited	Welland	ON	0.011	0.000	0.000	0.000	0.011
4603	Anchor Lamina Inc.	Cambridge	ON	0.011	0.000	0.000	0.000	0.011
5724	P&F Tool and Die II	Concord	ON	0.000	0.000	0.000	0.000	0.011
5756	Husky Injection Molding Systems Ltd	Bolton	ON	0.011	0.000	0.000	0.000	0.011
5982	Faurecia Automotive Seating Canada Ltd.	Mississauga	ON	0.000	0.000	0.000	0.000	0.011
1464	Imperial Oil	Sarnia	ON	0.010	0.000	0.000	0.000	0.010
2750	Camco Inc.	Hamilton	ON	0.010	0.000	0.000	0.000	0.010
4604	Anchor Lamina Inc.	Mississauga	ON	0.010	0.000	0.000	0.000	0.010
5968	Durham Furniture Inc.	Chesley	ON	0.000	0.000	0.000	0.000	0.010
3476	DaimlerChrysler Corporation	Windsor	ON	0.009	0.000	0.000	0.000	0.009
4845	Parrsboro Metal Fabricators Limited	Parrsboro	NS	0.009	0.000	0.000	0.000	0.009
5735	Dana Brake Parts Canada Inc.	Mississauga	ON	0.009	0.000	0.000	0.000	0.009
5766	Russel Metals Inc.	Burlington	ON	0.009	0.000	0.000	0.000	0.009
5827	Ontario Engineered Suspensions Ltd.	Blenheim	ON	0.009	0.000	0.000	0.000	0.009
5830	Massiv Die-Form Racktec	Brampton	ON	0.000	0.000	0.000	0.000	0.009
2580	Master Precision Tool &Die	Scarborough	ON	0.000	0.000	0.000	0.000	0.008
3886	Essex Manufacturing	Windsor	ON	0.000	0.000	0.000	0.000	0.008
5572	Fetichem inc	St-Michel de Napierville	QC	0.008	0.000	0.000	0.000	0.008
5958	IMT Corporation	Ingersol	ON	0.008	0.000	0.000	0.000	0.008
5969	Nelson Industrial Inc	Pickering	ON	0.000	0.000	0.000	0.000	0.008
5978	Fleetwood Metal Industries	Otterville	ON	0.008	0.000	0.000	0.000	0.008

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
2591	Pullmatic Mfg	Markham	ON	0.000	0.000	0.000	0.000	0.007
3766	General Motors of Canada Limited	London	ON	0.007	0.000	0.000	0.000	0.007
4605	Reliance Steel Fabricators Ltd.	Tilbury	ON	0.007	0.000	0.000	0.000	0.007
5649	Kaiser Aluminum & Chemical of Canada Ltd	London	ON	0.000	0.000	0.007	0.000	0.007
1400	Newmont Canada Limited	Marathon	ON	0.006	0.000	0.000	0.000	0.006
2574	Slide-Master	Newmarket	ON	0.000	0.000	0.000	0.000	0.006
2681	Normark Manufacturing	Concord	ON	0.000	0.000	0.000	0.000	0.006
4891	TKA Fabco Corp.	Ridgetown	ON	0.003	0.003	0.000	0.000	0.006
5015	PEI Energy Systems	Charlottetown	PE	0.006	0.000	0.000	0.000	0.006
5725	Formet Industries	St Thomas	ON	0.006	0.000	0.000	0.000	0.006
5981	Faurecia Automotive Seating Canada Ltd.	Bradford	ON	0.000	0.000	0.000	0.000	0.006
0231	Delhi Industries Inc	Delhi	ON	0.005	0.000	0.000	0.000	0.005
4045	Stelwire Ltd.	Hamilton	ON	0.000	0.005	0.000	0.000	0.005
4625	Ventra Group Inc	Tottenham	ON	0.005	0.000	0.000	0.000	0.005
5601	Bombardier Transportation	Thunder Bay	ON	0.005	0.000	0.000	0.000	0.005
5696	Russel Metals	Winnipeg	MB	0.005	0.000	0.000	0.000	0.005
0043	BASF Canada	Georgetown	ON	0.000	0.000	0.000	0.000	0.004
3983	Stackpole Ltd.	Mississauga	ON	0.004	0.000	0.000	0.000	0.004
4505	Ground Effects Ltd.	Windsor	ON	0.004	0.000	0.000	0.000	0.004
5825	Massiv Die-Form	Brampton	ON	0.004	0.000	0.000	0.000	0.004
5976	Fleetwood Metal Industries	Tillsonburg	ON	0.004	0.000	0.000	0.000	0.004
5977	Fleetwood Metal Industries	Tilbury	ON	0.004	0.000	0.000	0.000	0.004
7105	De Biasi & Associates Manufacturing	Mississauga	ON	0.000	0.000	0.000	0.000	0.004
7144	Titan Tool & Die Ltd.	Windsor	ON	0.004	0.000	0.000	0.000	0.004
7147	Atlantic Tube & Steel Inc.	Mississauga	ON	0.000	0.000	0.000	0.000	0.004
3019	Rollstamp	Concord	ON	0.003	0.000	0.000	0.000	0.003

Table A-1 Emissions of Manganese and its Compounds According to NPRI (NPRI, 2002) (continued)

NPRI ID	Company	City	Province	Emissions of Manganese and Its Compounds (tonnes)				
				Air	Water	Land	Underground	Total
4726	BASF Canada	Abbotsford	BC	0.000	0.000	0.000	0.000	0.003
4768	KMS Peel Inc.	Brampton	ON	0.003	0.000	0.000	0.000	0.003
7104	De Biasi & Associates Manufacturing	Mississauga	ON	0.000	0.000	0.000	0.000	0.003
3951	Downsview Stampings	Concord	ON	0.000	0.000	0.000	0.000	0.002
4368	Prévost Car Inc.	Ste-Claire	QC	0.000	0.000	0.000	0.000	0.002
5637	Dana Canada Inc.	St. Mary's	ON	0.002	0.000	0.000	0.000	0.002
5722	M. S. M.	Woodbridge	ON	0.000	0.000	0.000	0.000	0.002
5875	Skyjack Inc.	Georgetown	ON	0.002	0.000	0.000	0.000	0.002
5956	R. Reininger & Sons Ltd.	Newmarket	ON	0.000	0.000	0.000	0.000	0.002
5992	Aradco Management Ltd.	Windsor	ON	0.002	0.000	0.000	0.000	0.002
7123	Orion Bus Industries	Mississauga	ON	0.002	0.000	0.000	0.000	0.002
7152	Techform Products Limited	Penetanguishene	ON	0.000	0.000	0.000	0.000	0.002
1417	Roche Vitamins Canada Inc.	Cambridge	ON	0.000	0.000	0.001	0.000	0.001
2938	Zinc électrolytique du Canada Ltée	Valleyfield	QC	0.001	0.000	0.000	0.000	0.001
3071	Sunoco Inc.	Sarnia	ON	0.001	0.000	0.000	0.000	0.001
3231	General Motors of Canada Limited	St. Catharines	ON	0.001	0.000	0.000	0.000	0.001
4752	Knoll North America Corp.	Woodbridge	ON	0.000	0.000	0.000	0.000	0.001
5072	Shur Gain a div. of Maple Leaf Foods	Truro	NS	0.000	0.000	0.001	0.000	0.001
5654	Ventra Group Inc.	Cambridge	ON	0.001	0.000	0.000	0.000	0.001
5680	Russel Metals Inc.	Regina	SK	0.000	0.000	0.001	0.000	0.001
5681	russel metals inc	lachine	QC	0.001	0.000	0.000	0.000	0.001
5697	Welded Tube of Canada Limited	Concord	ON	0.000	0.000	0.000	0.000	0.001
5698	Welded Tube of Canada Limited	Concord	ON	0.000	0.000	0.000	0.000	0.001
5770	Splitcraft	Concord	ON	0.000	0.000	0.000	0.000	0.001
5889	Ventra Group Inc.	Bradford	ON	0.001	0.000	0.000	0.000	0.001
5940	Algonquin Automotive Huntsville	Huntsville	ON	0.001	0.000	0.000	0.000	0.001
5983	Faurecia Automotive Seating Canada Ltd.	Toronto	ON	0.000	0.000	0.000	0.000	0.001
7149	Yachiyo of Ontario Mfg., Inc.	Barrie	ON	0.000	0.000	0.000	0.000	0.001